Low energy effective Hamiltonians for strongly-correlated organic metals

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There are two jointly-authored works contained in this thesis, appearing in large part as Chapters 3 and 4, both of which I am first author. The second author of both papers is my principal supervisor, Prof. Ben Powell. The articles have been edited to remove Ben’s contributions as much as possible, which comprise parts of the introductory section and the discussion of the implications of our results. I performed all the research work reported in both papers. Additional material has been included to expand on the discussion of the relevant technical procedures.
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I performed all of the significant technical procedures, data analysis and research work reported in my thesis.

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No part of this thesis has been submitted to qualify for the award of another degree.

Published Works by the Author Incorporated into the Thesis


Additional Published Works by the Author Relevant to the Thesis but not Forming Part of it

None.
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Abstract

Strongly-correlated electronic materials can exhibit richly featured phase diagrams, including a Mott metal-insulator transition. In two particular classes of material, \( \kappa \text{-ET}_2 \text{X} \) and \( \beta' \text{-X[Pd(dmit)$_2$]}_2 \), the conducting side of this phase transition may contain superconducting and non-Fermi liquid metallic states, as well as the more usual Fermi liquid metallic state. The insulating side of the transition is often antiferromagnetic. However, in some of these materials more exotic states emerge such as spin liquids and valence bond crystals. These unusual insulating states are related, among other considerations, to the subtle changes in geometry among the crystal lattices of these materials, and the implications for the electronic structure.

These two materials both have a quasi-2D layered salt crystal structure whose layers can be described as an anisotropic triangular lattice. Each lattice site contains two organic units (ET or dmit) stacked into dimers stabilised by \( \pi - \pi \) intermolecular bonding. The dimers donate (ET) or accept (dmit) one electron from their counterions in the salt crystal, resulting in half-filled electronic systems.

One of the implications of strong electron correlation is that typical first-principles techniques in quantum chemistry, such as Hückel methods or density functional theory (DFT) using approximate exchange-correlation functionals, do not capture the qualitative physics of strongly-correlated systems. While DFT does not directly capture strongly-correlated phenomena, it is still effective at finding the parameters of low energy effective Hamiltonians describing these materials. Therefore, I studied the tight-binding and Hubbard models to explore the correlation between the model parameters and the electronic nature of each material. This work contributes to a greater goal of predicting from first principles calculations the low temperature states of these materials from the ground states of the relevant models.

I calculated the effective Coulomb repulsion between electrons/holes, \( U_m^{(v)} \), and site energy for an isolated ET molecule \textit{in vacuo}. \( U_m^{(v)} = 4.2 \pm 0.1 \text{ eV} \) for 44 experimental geometries taken from a broad range of conformations, polymorphs, anions, temperatures, and pressures (the quoted ‘error’ is one standard deviation). Hence \( U_m^{(v)} \) is essentially the same for all of the compounds studied. This shows that the strong (hydrostatic and chemical) pressure dependence observed in the phase diagrams of the ET salts is not due solely to \( U_m^{(v)} \). Therefore,
if the Hubbard model is sufficient to describe the phase diagram of the ET salts there must be significant pressure dependence on the intramolecular terms in the Hamiltonian and/or the reduction of the Hubbard $U$ due to the interaction of the molecule with the polarisable crystal environment.

The renormalised value of $U_m^{(v)}$ is significantly smaller than the bare value of the Coulomb integral: $F_0 = 5.2 \pm 0.1$ eV across the same set of geometries. This emphasises (i) the importance of using the renormalised value of $U_m^{(v)}$ and (ii) that a site in the Hubbard model does not correspond to any real orbital in the ET molecule as the orbitals change significantly, even in the isolated molecule, as the charge fluctuates. The site energy (for holes), $\xi_m = 5.0 \pm 0.2$ eV, varies only a little more than $U_m^{(v)}$ across the same set of geometries. However, the site energy plays a key role in understanding the role of disorder in ET salts in general and in particular the difference between the $\beta_L$ and $\beta_H$ phases of $\beta$-ET$_2$I$_3$.

The next parameterisation step I performed was an extension of the model to two sites, to calculate the interactions between holes in ET dimers for 23 experimental geometries taken from a range of materials in both the $\beta$ and $\kappa$ polymorphs. I find that the effective Coulomb interactions are essentially the same for all of the compounds studied. My parameterisation disagrees with similar reported parameterisations from the literature, which used both DFT and Hückel methods. This is caused by the failure of an assumption made in previous calculations (which estimate the effective Coulomb interaction from the intra-dimer hopping integral). I subsequently use my parameterisation results to explain a number of phenomena caused by conformational disorder in these materials.

Finally, I parameterised the tight-binding model for $\kappa$-ET$_2$Cu$_2$(CN)$_3$ and eleven $\beta'$ dmit materials. The ratio of the tight-binding parameters, $t'/t$, provides a measure of the geometric frustration present in the lattice. The materials studied range in $t'/t$ from 0.7–1.5, with one outlying crystal, $\beta'$-Et$_3$Me$_1$N[Pd(dmit)$_2$]$_2$, which has $t'/t \sim 0.33$ and has the typical antiferromagnetic insulating state. Of the materials with an unusual insulating state, the spin liquid $\beta'$-Et$_1$Me$_3$Sb[Pd(dmit)$_2$]$_2$ has $t'/t = 0.79$ while the valence bond crystal $\beta'$-Et$_1$Me$_3$P[Pd(dmit)$_2$]$_2$ has $t'/t = 0.87$. These parameter values are in the expected range for frustrated spins on an anisotropic triangular lattice in the model Hamiltonians that represent these materials. The presence of a glide plane symmetry in the layering direction of
many of the dmit materials produces a band structure in which two bands cross the Fermi energy, one for each distinct layer. In some materials, the bands may have a small energy separation, implying the half-filled electronic system is actually half-filled on average, with each band having an effective doping away from half-filling. This effect is on the order of 1%, but can have implications for the ground state of the relevant model Hamiltonians.
Keywords

strong correlations, BEDT-TTF, dmit, organic metals, Mott insulators, low energy effective Hamiltonians, quantum chemistry, DFT

Australian and New Zealand Standard Research Classifications (ANZSRC)

020201 Atomic and Molecular Physics — 20%.
020403 Condensed Matter Modelling and Density Functional Theory — 80%.
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2.1 Band structures of a metal (left) and an insulator (right). The only difference between these examples is the location of the bands relative to the Fermi energy, $E_F = 0$. In a metal, at least one band crosses $E_F$, making the band partially filled. In this case, $E_F$ is well-defined as the convergence of the ionisation potential and the electron affinity. At zero temperature, $E_F$ is also the chemical potential, $\mu$. By contrast, an insulator contains only filled and empty bands, i.e. no band crosses $E_F$. In this case, $E_F$ is not well-defined, and may be taken as either the ionisation potential (the top of the filled band), the electron affinity (the bottom of the empty band), or some point in between (as shown, sometimes seen in computational results or simply the average of the extremes).

2.2 The phase diagrams of the cuprates (left) and the $\kappa$-ET$_2$X salts (right) are remarkably similar. Both have a metal-insulator transition, superconducting states, and non-Fermi liquid metallic states. Of particular note is that the metal-insulator transition may be driven by doping (cuprates) or pressure (ET) as well as temperature. Zero doping on the cuprate phase diagram corresponds to half-filling (one electron per lattice site). As the doping increases (in the direction shown here), electrons are removed from the system such that, in the optimal doping region, there are 0.8 electrons per lattice site. The cuprate phase diagram is from Batlogg,[13] and the $\kappa$-ET$_2$X phase diagram is updated from Powell.[7]

2.3 ET (left) and Pd(dmit)$_2$ (right) molecules have structural similarities. Both are conjugated organic compounds with sulphur substitutions. Both structures interact with neighbouring units in the crystals through $\pi - \pi$ molecular orbital interactions, which favour stacking of the organic units typically 3.5 – 4.5 Å apart.[16] ET molecules may occur in different conformations, labelled here as staggered and eclipsed. The difference lies in the relative orientation of the terminal ethylene groups at the ends.
2.4 The $\beta$ (left) and $\kappa$ (right) polymorphs of ET crystals have a dimerised structure. This allows both structures to be treated as an anisotropic triangular lattice with an ET dimer on each lattice site. The anisotropic triangular lattice is shown by the lattice site connections and the hopping integrals, $t_1$ and $t_2$, that represent the energy associated with electrons hopping from one lattice site to a neighbouring site.

2.5 $\beta$-ET$_2$I$_3$ (left)[21] and $\beta'$-EtMe$_3$P[Pd(dmit)$_2$]$_2$ (right)[22] both possess a quasi-2D layered structure. Furthermore, within each layer the structures continue to resemble each other, with a common motif of organic molecules arranged into dimers, and aligned into an anisotropic triangular lattice structure. Note that the organic units are slanted relative to the crystal axes, producing an offset in the overlap between neighbouring dimers. Colour indicates symmetry equivalence within the unit cell. In this case, $\beta$-ET$_2$I$_3$ has only an inversion symmetry, whereas $\beta'$-EtMe$_3$P[Pd(dmit)$_2$]$_2$ contains one distinct cation and one Pd(dmit)$_2$ monomer, from which the other member of the dimer is derived by inversion symmetry, and two distinct cations. The Pd(dmit)$_2$ dimers are related by an inversion symmetry within layers and by a screw rotation symmetry in alternating layers. Images rendered in Mercury.[23]

2.6 The tight-binding model in one dimension produces a simple dispersion relation $E = \mu - 2t \cos(k_a)$. The Fermi surface is the $N-1$ dimensional surface of $E = \mu$. For the one dimensional case, this is simply two points, or one if $\mu$ corresponds to the bottom or top of the band.

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2.9 Schematic of the Hubbard models studied for the ET salts. The left panel shows the two site extended Hubbard model. Here each site represents a monomer. The Coulomb interactions ($U_m$ between electrons on the same monomer and $V_m$ between electrons on different monomers) and the hopping integral, $t$, are marked. The right panel shows the dimerised model. As the bonding orbital is filled only a single state is relevant, thus the only parameter is the effective Coulomb repulsion between electrons/holes in that state, $U_d$. This model does not extend to the Pd(dmit)$_2$ materials, where the interactions of other monomer orbitals must be accounted for.

2.10 VASP (left) and Quantum-espresso (right) are both plane-wave based DFT codes. The two are compared here with a band structure of simple crystalline copper, calculated in a GGA. The two results agree qualitatively and quantitatively, despite differences that emerge due to discretisation, the type of exchange-correlation functional, and the construction of the pseudopotentials. The discrepancy in the position of the Fermi energy between the graphs is most likely due to different input conditions regarding how the density of states is calculated. In both cases, the Fermi energy $E_F$ is found by satisfying $\int_{-\infty}^{E_F} D(E)dE = N$, where $D(E)$ is the density of states per unit energy and $N$ is the number of valence electrons per unit cell.
3.1 Dependence of the energy of an ET molecule on the charge of the molecule. Two different geometries are studied. The ‘frozen’ geometry is relaxed from that found experimentally[21] in $\beta$-(ET)$_2$I$_3$ in the neutral charge state and then held fixed during the self-consistent field (SCF) calculations at different charge states. For the ‘relaxed’ data the nuclear geometry is relaxed separately for each charge state. The energies are exactly equal by definition in the charge neutral state; for other charge states the nuclear relaxation lowers energies. This reduces the curvature of $E(q)$, i.e., lowers $U^{(v)}_{mc}$ and hence $U^{(v)}_m$. It can be seen that for both the ‘frozen’ and the ‘relaxed’ geometries the energy of the fractional charge states is extremely well described by the classical quadratic functions, Eqs. (3.8). In contrast it is known that for the exact functional the energy of molecules with fractional charges is a linear interpolation between the integer charge states.[82–85] To an excellent approximation $U^{(v)}_{mc} = U^{(v)}_m$ whereas $\epsilon_{mc}$ and $\xi_{mc}$ are not good approximations to $\epsilon_m$ and $\xi_m$. In contrast for the exact functional $\epsilon_m = \epsilon_{mc}$, $\xi_m = \xi_{mc}$, and $U^{(v)}_{mc} = 0$. This incorrect result is a manifestation of the delocalisation error of DFT and closely related to the band gap problem.[83–88] These calculations use TZP basis sets and TM2 pseudopotentials.

3.2 The eclipsed and staggered conformations of the ET molecule. The major difference is the relative orientation of the terminal ethylene groups.
3.3 Orthographic projections of the isosurface of the HOMO of the ET molecule in ‘experimental’ geometries taken from (a) eclipsed $\beta$-(ET)$_2$I$_3$, (b) staggered $\beta$-(ET)$_2$I$_3$, and (c) $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl. Note the great similarity of the HOMOs corresponding to the ‘experimental’ geometries from eclipsed and staggered $\beta$-(ET)$_2$I$_3$ and the small electronic density on the terminal ethylene group, which is involved the change between the eclipsed and staggered conformations. Further, the HOMOs of the ET molecule in the ‘experimental’ geometries taken from $\beta$-ET$_2$I$_3$ and $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl are remarkably similar despite the fact that this geometry is taken from a different crystal polymorph with a different anion. This is consistent with my finding that the changes in the conformation of the ET molecule, in different polymorphs and in crystals with different anions, do not significantly affect $U_{m}^{(v)}$. Colour indicates the sign of the Kohn-Sham orbital. All isosurfaces are $\pm 0.07 \AA^{-3/2}$ and calculated in the charge-neutral state. These calculations use TZP basis sets and TM2 pseudopotentials. Animations showing different isosurfaces are available online.[128] .......................... 57

3.4 The effective Coulomb repulsion between electrons/holes, $U_{m}^{(v)}$, on an ET monomer in the ‘experimental’ geometries corresponding to different anions, conformations (eclipsed offset to the left, staggered to the right), temperatures, pressures, and crystal polymorphs. Note the limited range (3.9 – 4.4 eV) of the ordinate. $U_{m}^{(v)}$ does not change significantly across the different (ET)$_2$X crystals and has a mean value of 4.2 $\pm$ 0.1 eV. The calculations use TZP basis sets and TM2 pseudopotentials. .......................... 58

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4.1 The HOMO of (ET)$_2^{2+}$ (top) and charge neutral (ET)$_2$ (bottom), with nuclear positions from the crystal $\beta$-(ET)$_2$I$_3$. The HOMO of (ET)$_2^{2+}$ is the dimer bonding orbital and the HOMO of (ET)$_2$ is the antibonding orbital of the two ET HOMOs (cf. Fig. 4.3). The essential difference between the two lies in the relative phase of the orbital function on each molecule. The bonding orbital connects the ET molecules at the S···S contacts (cf. Fig. 3.2). In the antibonding orbital, there are nodes between the S···S contacts.

4.2 The HOMO of (ET)$_2^{2+}$ (top) and charge neutral (ET)$_2$ (bottom), with nuclear positions from the crystal $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$. The similarity of the nuclear structures and orbitals between this conformation and the $\beta$ conformation in Fig. 4.1 highlight the dimer as a common structural unit within two different packing motifs.

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4.8 Inter-monomer $V_m^{(v)}$ for various ET dimers. For $\beta$-(ET)$_2$X crystals, $V_m^{(v)} = 2.69 \pm 0.13$ eV and for $\kappa$-(ET)$_2$X crystals, $V_m^{(v)} = 2.72 \pm 0.09$ eV. The mean value is $V_m^{(v)} = 2.71 \pm 0.10$ eV. The difference in $V_m^{(v)}$ between the crystal polymorphs is $\sim 2\%$. Therefore, $V_m^{(v)}$, like $U_d^{(v)}$, does not significantly depend on the geometry associated with crystal polymorph. The effect of ET conformation on the value of $V_m^{(v)}$ in the crystals $\beta$-(ET)$_2$I$_3$ and $\kappa$-(ET)$_2$Cu[N(CN)$_2$I$_3$] is also similar to the effect on $U_d^{(v)}$. $V_m^{(v)}$ is lowest when the ET dimer has the staggered-staggered conformation, and rises when either or both ET molecules are eclipsed.
5.1 The lattice sites of the conducting layer of $\kappa$-ET$_2$Cu$_2$(CN)$_3$ depend on whether the model contains hopping integrals among monomers (left) or dimers (right). In the monomer model, $t_1$ is the intradimer interaction and is typically strongly stabilised by $\pi - \pi$ intermolecular bonding. This makes $t_1$ much larger in magnitude than other $t$ parameters, and separates the four bands of the model into two well-separated pairs. The dimer model would reproduce only the pair of bands nearest the Fermi energy. Note the reduction of parameters, $t' = t_3/2$ and $t = (t_2 + t_4)/2$, required to convert from a monomer model to a dimer model. If $t_1$ is large, little is lost in terms of fitness of the model because $t_1$ is effectively integrated out of the Hamiltonian. Note also the presence of a screw rotation symmetry within the conducting plane. This has the effect of enforcing the symmetry of the two $t$ parameters in the dimer model. This symmetry is absent in the $\beta'$-dmit materials, requiring the relevant dimer model to separate the two $t$ hops into independent parameters. Image from Kandpal et al. [167].

5.2 (left) A simple unit cell, with two sublattices coloured red and black and two hopping interactions, $t$ and $t'$. A Hamiltonian matrix element would look like $te^{i\mathbf{k}\cdot\mathbf{r}} + t'e^{i\mathbf{k}\cdot\mathbf{r}'}$. (right) The same unit cell, but each sublattice has undergone a phase rotation $e^{i\phi_A}$ and $e^{i\phi_B}$, respectively, such that the $t$ interaction has no phase and the $t'$ interaction has direction $\mathbf{r}_t = -\mathbf{a}$. The Hamiltonian matrix element is now $t + t'e^{-i\mathbf{k}\cdot\mathbf{a}}$. The most significant result of this transformation is that the hopping terms no longer depend on the length or direction of the physical hops. All hopping interactions have either $\mathbf{r}_t = 0$ or an integer linear combination of lattice vectors.

5.3 Espresso band structure (blue) and tight-binding fit for a monomer lattice (green) for $\kappa$-ET$_2$Cu$_2$(CN)$_3$. $t'/t = 0.84$ (see Table (5.1). The resultant band structure is an excellent fit to the DFT band structure. This process shall be repeated below for several $\beta'$-dmit materials.
5.4 The three basic structures of the dmit materials studied here. (a) The dimer unit has a translation symmetry with every other dimer unit. (b) The dimer has a translation symmetry with other dimers in its layer, but is related to neighbouring layers by a glide plane symmetry. The layers are connected (the smaller lattice sites are in the layer behind the larger) by an interlayer hopping, $t_\perp$. Note this increase of the size of the unit cell in the layering direction decreases the FBZ in the relevant direction in $k$-space. (c) There are two dimers per layer that are not related by a translation symmetry, as well as a screw rotation symmetry between the neighbouring layers.

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5.6 The DFT band structure and tight-binding fits for As-0 (a), As-2 (b) and Cs (c). Note that the Cs band structure is for a room temperature crystal structure. The band structures and Fermi surfaces are marginally different among these materials. $t'/t = 1.42$ for As-0, compared to 1.26 for As-2 and 0.93 for Cs. The fit for Cs is relatively poor, but the poor fit is localised to features not near $E_F$. The fit is reasonably good near $E_F$, so the associated Fermi surfaces are not significantly affected. The bands of As-2 feature avoided crossings, resulting in the tilted shape of the Fermi surface. The crossover points are visible in the band structure, in the vicinity of V and X. These crossovers are absent in the other two band structures.
5.7 The DFT band structure and tight-binding fits for P-0 (a) and P-2 (b & c). Note that the P-2 band structures are from crystal structures measured at room temperature. At low temperatures, P-2 adopts the third type of crystal structure, similar to P-1, and most likely undergoes significant changes to the tight-binding parameters. All three of these structures have avoided band crossings, evidenced by the crossing Fermi surfaces. P-0 actually has one band crossing the FBZ boundary in the Y direction, indicating a relatively strong quasi-1D character. $t'/t = 1.48$ for P-0, which is the highest $t'/t$ of the materials studied.

5.8 The DFT band structure and tight-binding fits for Sb-0 (a) and Sb-2 (b). Note that the Sb-2 band structure is for a room temperature crystal structure. At low temperature, Sb-2 adopts the same type of crystal structure as P-1 and most likely undergoes significant changes to the tight-binding parameters. Both materials have avoided crossings, with Fermi surfaces slanted towards Y (Sb-0) and M (Sb-2). It is interesting to note that these two materials are substantially above (Sb-0, $t'/t = 1.23$) and below (Sb-2, $t'/t = 0.72$) the frustrated region, but their band structures and Fermi surfaces are more similar to each other than most other materials compared here in this way.
5.9 The band structure and Fermi surface (a) of Sb-1 are quite similar to the other type 2 dmit materials studied here. However, the separation between the bands is quite small, especially in the M-V-Y region of the band structure, where most of the dmit materials have some asymmetric features and more rapidly varying energy differences between the bands at \( k \)-points in that region. This results in a Fermi surface with avoided crossings, like several of the other materials, but with a substantially smaller separation between the Fermi surfaces in \( k \)-space. Doubling the unit cell in the conducting plane yields a folded down band structure and Fermi surface (b), due to the reduced FBZ. This downfolded band structure allows a more direct comparison between the electronic structure of Sb-1 and that of P-1 (see Figure (5.10)) and \( \kappa \)-ET\(_2\)Cu\(_2\)(CN)\(_3\) (see Figure (5.3)). Of particular note is the emergence of secondary orbits (red and black lines) formed from the edge of the downfolded Fermi surface. These regions actually represent a third and fourth band crossing the Fermi energy, but only in the region of \( k \)-space near Z.
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5.11 (Left) The relationship between $t'/t$ and the transition temperature to the antiferromagnetic insulating state (a-f), the absence of a phase transition as low as several mK (g), and the transition of P-1 to the valence bond crystal state (h), as collected by Shimizu et al. seems very straightforward from model parameterisations using Hückel methods (left).[186] However, my parameterisation of the tight-binding model from the DFT band structure (right) shows that the relationship is more complicated. The antiferromagnets (a-f on Shimizu’s graph and the black circles on mine) are present in my graph in the same region of parameter space as the spin liquid Sb-1 and the valence bond crystal P-1 (g and h on Shimizu’s graph, respectively). $t'/t$ alone is insufficient to characterise their different insulating states, other phenomena besides the hopping integrals influence both the low temperature physics of the materials and a more sophisticated Hamiltonian would consider more of these variables.
3.1 Comparison of different methods of calculating the effective monomer on-site Coulomb repulsion for ET. No significant differences are found between $U^{(v)}_{mc}$ and $U^{(v)}_m$ from the DFT calculations. This result has been confirmed for all of the geometries studied below. Further, no significant differences are found between the two conformations. $F_0$ is significantly larger than $U^{(v)}_m$, in qualitative agreement with previous results from wavefunction based methods (c.f. Table 3.2). The nuclear geometry is that seen ‘experimentally’ in $\beta$-(ET)$_2$I$_3$ for both the eclipsed and staggered conformations. The calculations use TZP basis sets and TM2 pseudopotentials. All values are in eV.

3.2 Previously reported calculations of the Coulomb energy ($F_0$ and $U^{(v)}_m$) of ET. These calculations were performed at various levels of theory, using various basis sets and with geometries taken from x-ray crystallography experiments on various different materials. $F_0$ is significantly larger than $U^{(v)}_m$, consistent with my results. I make use of the following abbreviations in the above table: HF (Hartree-Fock); RHF (restricted Hartree-Fock); and VB (valence bond). Fortunelli and Painelli[111–113] calculated $F_0$ for ET dimers in different charge states, $q$. All energies are in eV.

3.3 Pseudopotential parameters for the TM2 pseudopotentials used in SIESTA calculations were generated with the ATOM utility. These are the input parameters, taken from the header of the .psf files that were created. All pseudopotentials were generated by ATOM version 3.2.2, set for use with the PBE exchange-correlation functional, with no relativistic correction. The carbon pseudopotential uses ‘pcec’ pseudocore-correction. Hydrogen and sulphur do not use core corrections. Spin polarisation was not used. The electron population, $n$, and convergence radii, $r$, for each angular momentum state follow.
3.4 Calculated bare and renormalised parameters for the Hubbard model for ET monomers under various geometry relaxation schemes and with different pseudopotentials, basis sets and codes (see section 3.2). The ‘experimental’ geometry is that reported for an ET molecule in $\beta$-(ET)$_2$I$_3$,\cite{21} measured at 298 K, with the H atom (not observed in x-ray crystallography) positions relaxed. The ‘frozen’ coordinate system was relaxed in the charge neutral state and held fixed for other charge states. The ‘relaxed’ geometry was optimised at every charge state. All geometry relaxations were carried out in calculations using TZP basis functions and TM2 pseudopotentials; I have also carried out the relaxations in using the other methods in the table and find no significant differences. The abbreviation pseudo. (for pseudopotential) is used in this table and others below. The RMSE is taken from the fit to the classical Eqs (3.8). All values are in eV. .............................................................. 55

3.5 Calculated bare and renormalised parameters for the Hubbard model for an ET molecule at the ‘experimental’ geometry observed at ambient temperature and pressure in various polymorphs of (ET)$_2$I$_3$. The changes in conformation due to the crystal packing structure do not have a large effect on the value of $U_m^{(v)}$. The calculated $\xi_m$ is larger for the $\beta$ polymorph than the others explored, indeed $\xi_m$ varies by less than 1% among the other polymorphs. Note that there is a significant difference between the values of $\xi_m$ in the eclipsed and staggered conformations in the $\beta$ phase. This is consistent with the effects of conformational disorder on $\beta$-ET$_2$I$_3$,\cite{122} The calculations use TZP basis sets and TM2 pseudopotentials. All values are in eV. ................. 56
3.6 Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of $\alpha$-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, X taken at a range of temperatures, T. The structural data obtained by Bender et al.\cite{90} and Emge et al.\cite{91} contains three distinct monomer structures, one staggered and two eclipsed. The eclipsed conformations are numbered arbitrarily in order to distinguish them. The calculations use TZP basis sets and TM2 pseudopotentials. 56

3.7 Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of $\beta$-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, X. The calculations use TZP basis sets and TM2 pseudopotentials. 58

3.8 Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of $\beta''$-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, X and was taken at various temperatures, T (temperatures in K). The calculations use TZP basis sets and TM2 pseudopotentials. 59

3.9 Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of $\kappa$-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, X and was taken at various pressures, P, and temperatures, T (temperature in K). The calculations use TZP basis sets and TM2 pseudopotentials. 61
3.10 Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of θ-(ET)$_2$X monomers. Two distinct monomers were observed experimentally,[93] they are labelled arbitrarily above but appearing in the crystal in alternating positions. The calculations use TZP basis sets and TM2 pseudopotentials.

4.1 Previous estimates of $U_d^{(v)}$ for various β- and κ-phase ET salts. These values were obtained from both Hückel and density functional methods under the assumptions $U_m^{(v)} \to \infty$ and $V_m^{(v)} = 0$, which yields $U_d^{(v)} = 2t$. These estimates substantially underestimate the actual value of $U_d^{(v)}$ (see Fig. 4.6) as $U_m^{(v)} \sim V_m^{(v)}$. The two site extended Hubbard model produces values of $t$ on the same order of magnitude as these Hückel calculations. One should also note the wide scatter between the different Hückel calculations, even between different studies of the same material.
5.1 Tight-binding parameters for the tight-binding model of $\kappa$-ET$_2$Cu$_2$(CN)$_3$. The mapping from the monomer model parameter space, $t_{[1-4]}$, to the dimer model space, $t$ and $t'$, is $t = (t_2 + t_4)/2$ and $t' = t_3/2$. Zheng’s calculation of $t'$ has a substantial uncertainty range, arising from the uncertainty in the calculation of the spin interaction, $J$. This quantity was calculated from high-temperature series expansions of the magnetic susceptibility, and requires measurement of the temperature corresponding to peak susceptibility, $T_P$. The region of the curve in the vicinity of $T_P$ is unusually flat in $\kappa$-ET$_2$Cu$_2$(CN)$_3$, hence the reported uncertainty. Of particular significance is the quantity $t'/t$, which quantifies the anisotropy of the triangular dimer lattice. There is good agreement among all methods presented here. As $t'/t \rightarrow 1$, the lattice becomes more "frustrated", and such materials exhibit qualitatively different physics to crystals of nearly identical chemical and physical structure. For example, $t'/t = 0.84$ is close to frustration, and the Mott insulating state of $k$-CN has no ordering of spins on neighbouring lattice sites. However, many other $\kappa$-ET crystals exhibit an antiferromagnetic Mott insulating state. A crucial open question of this area is, what amount of frustration is required to drive a crystal from a spin-ordered insulating state to a spin liquid or other qualitatively different insulating state? 85

5.2 The tight-binding parameters for these dmit materials show a variety of model parameter values. All energies are in meV. $t_a$ is the average of the two closest $t_{[1-3]}$ and the remaining hopping integral becomes $t'$, to provide a result $t'/t_a$ that can be compared to $t'/t$ values in the literature for some of these materials. (See table 5.3 for this comparison.) The relative difference between the two $t_{[1-3]}$ is expressed in the quantity $\Delta t/t_a$, where $\Delta t$ is the difference between the two $t_{[1-3]}$. P-1 has two $t_\perp$ parameters, corresponding to two distinct hopping interactions between the sublattices in one layer and the sublattices in the neighbouring layers. 90
5.3 Several of the dmit compounds exhibit a temperature-driven metal-antiferromagnetic insulator transition at the listed temperatures. There is substantial disagreement between my tight-binding parameters and the ones Shimizu used, and this is reflected in the less simple relationship between $t'/t$ and the transition temperature $T$ (see Figure (5.11)). There are two P-2 structures studied in this work, which is why two $t'/t$ values are listed.
List of Abbreviations

Common Acronyms

BEDT-TTF. bis(ethylenedithio)tetrathiafulvalene.

BHS. Bachelet, Hamann and Schlüter, a method of generating pseudopotentials.

DFT. Density-functional theory.

DMIT. 1,3-dithiole-2-thione-4,5-dithiolate.

DMFT. Dynamical mean-field theory.

DZ. Double-ζ basis set.

DZP. Double-ζ plus polarisation basis set.

ET. See BEDT-TTF.

Et. Ethyl.

FBZ. First Brillouin zone.

GGA. Generalised gradient approximation.

HF. Hartree-Fock.

HOMO. Highest-occupied molecular orbital.

LDA. Local density approximation.

LSDA. Local spin density approximation.

LUMO. Lowest unoccupied molecular orbital.

Me. Methyl.

NRLMOL. Naval Research Laboratories MOLecular orbital package.
nD ........ n-dimensional.

PBE ........ Perdew, Burke and Erzenhof, a type of exchange/correlation functional used in DFT.

PP ........ Porezag-Pederson.

Pn ........ Pnictide.

Pn-n ....... Et$_n$Me$_{4-n}$Pn[Pd(dmit)$_2$]$_2$.

QZP ....... Quadruple-ζ plus polarisation basis set.

RHF ........ Restricted Hartree-Fock.

RMSE ...... Root mean square error.

SCF ........ Self-consistent field.

SIC ........ Self-interaction correction.

SIESTA...... Spanish Initiative for Electronic Simulations with Thousands of Atoms.


SZP .......... Single-ζ plus polarisation basis set.

TM2 ........ Improved Troullier-Martins pseudopotential.

TTF-TCNQ Tetrathiafulvalene tetracyanoquinodimethane.

TZP ........ Triple-ζ plus polarisation basis set.

VB-HF ...... Valence bond Hartree Fock.

VBC ....... Valence bond crystal.
Common mathematical notation

\( \hat{c}^{(1)}_{i\sigma} \) .......... Annihilation (creation) operator for an electron on site \( i \) in spin state \( \sigma \).

\( D(E) \) .......... Density of states.

\( E_F \) .......... Fermi energy.

\( eV \) .......... Electron volt, \( \approx 1.602 \times 10^{-19} \text{ J} \).

\( \hat{h} \) .......... A Hamiltonian.

\( \hat{h}^{(1)}_{i\sigma} \) .......... Annihilation (creation) operator for a hole on site \( i \) in spin state \( \sigma \).

\( \hbar \) .......... Planck’s constant, \( \hbar \approx 1.055 \times 10^{-34} \text{ m}^2\text{kg/s} \).

\( k_B \) .......... Boltzmann constant, \( k_B \approx 1.38062 \times 10^{-23} \text{ JK}^{-1} \).

\( \mu \) .......... Chemical potential, at zero temperature equal to \( E_F \). The Lagrange multiplier associated with conservation of particle number.

\( \mathbf{k}\)-path ........ A path travelled through \( \mathbf{k}\)-space.

\( \mathbf{k}\)-space .... The momentum space of a crystal’s reciprocal lattice.
Introduction

Strongly-correlated electronic systems exhibit a variety of interesting and unusual phenomena[3–7]. Of particular note is the presence of a high-temperature superconducting phase and a Mott metal-insulator transition[4]. The Mott transition is a phase transition between a metallic state and an insulating state.[8]

Strongly-correlated electronic systems are materials where electron-electron interactions are so strong that they cannot be represented accurately by an equivalent system of weakly interacting quasiparticles. The implementation of first-principles theoretical quantum chemistry techniques to describe and explain the behaviour of crystalline electronic conductors has long been constrained by the limits of these techniques to capture, even qualitatively, the physics of strongly-correlated electronic systems. An alternative approach to these problems is to use model Hamiltonians to capture the salient properties of these systems without the need for a complete and accurate first-principles description of the electronic properties of those systems.

One such type of material that benefits from such a model Hamiltonian approach are the quasi-2D layered organic charge transfer salts. Materials of this type based on the cation bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) have a feature-rich and interesting phase diagram, most of which is not captured by standard quantum chemistry methods such as density-functional theory (DFT). A similar physical crystal structure and low temperature phase diagram is present in the quasi-2D and quasi-1D layered crystals of the organic unit 1,3-dithiole-2-thione-4,5-dithiolate (dmit). This thesis describes the work I have performed
in applying a particular model Hamiltonian, the Hubbard model, to these crystals.

Chapter 2 contains the background material necessary to appreciate the results and analysis reported in later chapters. The chapter is divided into sections by broad topic. First I discuss the quantum theory of electrons in crystalline solids with a short introduction to one particular manifestation of strong electron correlations — the Mott metal-insulator transition. Then I shall discuss the physical properties of the ET and dmit crystals.

Afterwards, I introduce the effective low energy Hamiltonians used to describe the electronic behaviour of the crystalline solids studied, including the tight-binding and related Hubbard models. Finally, I discuss the technical process of calculating the parameters of the model Hamiltonians, using the highly successful density functional theory (DFT) and several of its computational implementations.

In chapters 3 and 4 I present the results of my DFT calculations on small clusters of ET molecules (monomers and dimers, respectively), and discuss the implications of these results for the overall goal of parameterising the Hubbard model for ET salts. These chapters are heavily based on articles published during the course of the project.[1, 2]

Chapter 5 considers the ongoing efforts reported in the literature continuing the parametrisation of a Hubbard model for ET crystals, and presents an example reproduction of one recently completed tight-binding parameterisation for $\kappa$-ET$_2$Cu$_2$(CN)$_3$. Then I implement the same techniques on dmit crystals and report the results.

In chapter 6 I summarise the work and present my conclusions.
2.1 Band structure theory and Mott insulators

2.1.1 Sommerfeld, Bloch and band structures

The first quantum mechanical description of the electronic properties of crystalline materials was proposed by Sommerfeld in 1928[9]. A key assumption made by the Sommerfeld model is that electrons do not interact with either the nuclei in the crystal or other electrons. Therefore, the wavefunction for these electrons is single-body, and takes the form of a plane wave

\[ \psi(r) = Ae^{ikr}. \]  

(2.1)

where \( A \) is a normalisation factor for the amplitude related to the volume of the crystal. The values of \( k \cdot r \) are quantised such that \( k_i = \frac{2\pi n_i}{L_i} \), where \( i \in \{x, y, z\} \), \( n_i \) is an integer and \( L_i \) is the length of the crystal in the \( i \) direction. This quantisation of available electronic states combined with the Pauli exclusion principle[10] implies the existence of a density of states per unit energy, and regions of \( k \)-space containing occupied and unoccupied electronic states, separated by Fermi surfaces.[11]

While the Sommerfeld model introduced several important concepts in condensed matter physics, it was not until Bloch refined the model to incorporate the effects of electrons’
interactions with a nuclear lattice that a quantum theory of condensed matter truly came into its own.

The Bloch model differs from the Sommerfeld model in two ways. First, the Schrödinger equation for the Bloch model contains a potential energy term, $V$, representing the Coulomb attraction from the nuclei

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V(x, y, z)) \psi = 0. \quad (2.2)$$

The other difference is that the solutions to this Schrödinger equation are not simply plane waves, but plane waves enveloped with a function, $u_k$, that shares the periodicity of the crystal lattice.

$$\psi_k = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(x, y, z). \quad (2.3)$$

The energy of solution $\psi_n(k)$ is $E_n(k)$, and it is commonplace to describe the electronic system of a crystal as a graph of $E$ vs $k$ along one dimensional sections of $k$-space (the $k$-path). This is called a band structure.

Band structures are a powerful tool for characterising the electronic properties of crystals. For example, they show the difference between metals and insulators in an intuitive way (see Figure (2.1)). If any band crosses the Fermi energy then the material is metallic. If the Fermi energy lies within a gap between bands, the material is an insulator. If a band crosses the Fermi energy, then there are unoccupied electronic states available to the system at infinitesimal energy excitations. In practice, the smallest energy excitations of the system would be thermal, i.e. on the order of $E \sim k_B T$, where $k_b$ is Boltzmann’s constant and $T$ is the temperature. In the case of an insulator, some finite amount of energy equal to the gap between the occupied and unoccupied bands is required to excite an electron. This energy would be much greater than $k_b T$. A semiconductor is essentially the same as an insulator, except the required excitation energy is not much greater than $k_b T$, and may even be zero in the case where a full band meets an empty band with no energy gap between them.
2.1 Band structure theory and Mott insulators

Figure 2.1: Band structures of a metal (left) and an insulator (right). The only difference between these examples is the location of the bands relative to the Fermi energy, $E_F = 0$. In a metal, at least one band crosses $E_F$, making the band partially filled. In this case, $E_F$ is well-defined as the convergence of the ionisation potential and the electron affinity. At zero temperature, $E_F$ is also the chemical potential, $\mu$. By contrast, an insulator contains only filled and empty bands, i.e. no band crosses $E_F$. In this case, $E_F$ is not well-defined, and may be taken as either the ionisation potential (the top of the filled band), the electron affinity (the bottom of the empty band), or some point in between (as shown, sometimes seen in computational results or simply the average of the extremes).
2.1.2 Mott insulators

Of course, band structure theory based on the Bloch model does not exactly capture the electronic behaviour of every known crystal. Some materials are insulators despite this theory predicting metallic states. In particular, some materials undergo a metal-insulator phase transition with some changing control parameter. For example, VO$_2$ and V$_2$O$_3$ undergo this transition as a function of temperature and pressure, whereas $(V_{1-x})_2O_3$ undergoes this transition as $x$ is varied. Other transition metal oxides are known to exhibit this phase transition and were the first compounds in which the phenomenon was discovered.[8][11].

Some decades later, Mott metal-insulator transitions were discovered in quasi-2D layered materials. This Mott transition has been observed in the cuprate superconductors (for an accessible review of the phase diagram of the cuprates, see [12]), and has been studied extensively not just for the interest in the metal-insulator transition phenomenon, but to provide indirect insight into the other states near the Mott transition on the cuprate phase diagram.

However, it is another type of layered material that is the primary focus of this thesis. Quasi-2D layered salts of the organic cation BEDT-TTF (ET), and of the organic anion Pd(dmit)$_2$, have a phase diagram similar to that of the cuprates. It contains metallic and non-metallic regions separated by a Mott transition, and even a superconducting phase in some ET crystals.

There are three experimental control parameters used to drive a material through its Mott transition. These are temperature, pressure, and doping. Doping applies to the cuprate materials, and refers to removing oxygen atoms from sites within the copper oxide layers. This has the effect of removing electrons from the system, and adjusts the filling of the electronic structure. (see Figure (2.3)).

2.1.3 (ET)$_2X$ and X[Pd(dmit)$_2$]$_2$ crystals

ET, or bis(ethylenedithio)tetrathiafulvalene is a synthetic organic molecule composed of carbon, sulphur and hydrogen atoms.[14] It is a heavily substituted member of the fulvalene family, a set of molecules based on two cross-conjugated rings connected by a bond.[15] The
2.1 Band structure theory and Mott insulators

Figure 2.2: The phase diagrams of the cuprates (left) and the $\kappa$-ET$_2$X salts (right) are remarkably similar. Both have a metal-insulator transition, superconducting states, and non-Fermi liquid metallic states. Of particular note is that the metal-insulator transition may be driven by doping (cuprates) or pressure (ET) as well as temperature. Zero doping on the cuprate phase diagram corresponds to half-filling (one electron per lattice site). As the doping increases (in the direction shown here), electrons are removed from the system such that, in the optimal doping region, there are 0.8 electrons per lattice site. The cuprate phase diagram is from Batlogg,[13] and the $\kappa$-ET$_2$X phase diagram is updated from Powell.[7]

ET crystals studied here form quasi-2D layered salts, each layer alternating between cation (ET) and anion.

Superconducting states in ET materials were discovered shortly before the discovery of superconductivity in the cuprates, (for example, superconductivity in $\beta$-ET$_2$I$_3$ was reported in 1985,[17] one year before the discovery of the first cuprate superconductor.[18] The cuprates quickly overshadowed the organics for research attention due to the higher temperature scale of the superconducting state in the cuprates. However, research interest in the organics has grown as new materials are discovered and characterised, and as computational power becomes ever more available for applying first-principles techniques to these materials, and as it becomes increasingly apparent that the natures of these two classes of material are related.

ET has many structural motifs, or polymorphs, which affect the electronic properties of the material. Of particular interest are the $\beta$ and $\kappa$ polymorphs (see Figure (2.4)), which feature a strong dimerisation of the ET molecules (see Figure (2.5) for an example of a $\beta$ structure). This has implications for the electronic properties, particularly for the band
Background theory

Figure 2.3: ET (left) and Pd(dmit)$_2$ (right) molecules have structural similarities. Both are conjugated organic compounds with sulphur substitutions. Both structures interact with neighbouring units in the crystals through $\pi - \pi$ molecular orbital interactions, which favour stacking of the organic units typically 3.5 – 4.5 Å apart.[16] ET molecules may occur in different conformations, labelled here as staggered and eclipsed. The difference lies in the relative orientation of the terminal ethylene groups at the ends.

Dmit, or 1,3-dithiole-2-thione-4,5-dithiolate is another synthetic organic molecule composed of carbon and sulphur. In the crystals studied here, the dmit combines with Palladium to form Pd(dmit)$_2$, which has a similar overall shape to an ET molecule. Again, the Pd(dmit)$_2$ arranges into stacks stabilised by $\pi - \pi$ interactions (see Figure (2.5)). Pd(dmit)$_2$ materials are less well-studied than the ET materials. However, the phases observed in Pd(dmit)$_2$ materials are similar to those of the ET and cuprate materials, including a metal-insulator transition and a superconducting state.[19, 20]

2.2 The tight-binding model

2.2.1 1D lattice — the linear chain

The Hamiltonian for the tight-binding model in one dimension is:

$$\hat{H}_{tb} = \mu \sum_{i \sigma} \hat{c}_{i \sigma}^\dagger \hat{c}_{i \sigma} - t \sum_{i \sigma} \left( \hat{c}_{i \sigma}^\dagger \hat{c}_{i+1 \sigma} + \hat{c}_{i+1 \sigma}^\dagger \hat{c}_{i \sigma} \right)$$  \hspace{1cm} (2.4)

where the $i$ and $i + 1$ indices denote nearest-neighbour interactions. If the lattice sites are separated by a distance $a = ae_i$ where $e_i$ is the unit vector in the direction of the chain, the site labelled $i$ is located at the position $r_i$, and the $i + 1$th site is located at position $r_{i+1} = r_i + a$. 

2.2 The tight-binding model

Figure 2.4: The $\beta$ (left) and $\kappa$ (right) polymorphs of ET crystals have a dimerised structure. This allows both structures to be treated as an anisotropic triangular lattice with an ET dimer on each lattice site. The anisotropic triangular lattice is shown by the lattice site connections and the hopping integrals, $t_1$ and $t_2$, that represent the energy associated with electrons hopping from one lattice site to a neighbouring site.

Figure 2.5: $\beta$-ET$_2$I$_3$ (left)[21] and $\beta'$-EtMe$_3$P[Pd(dmit)$_2$]$_2$ (right)[22] both possess a quasi-2D layered structure. Furthermore, within each layer the structures continue to resemble each other, with a common motif of organic molecules arranged into dimers, and aligned into an anisotropic triangular lattice structure. Note that the organic units are slanted relative to the crystal axes, producing an offset in the overlap between neighbouring dimers. Colour indicates symmetry equivalence within the unit cell. In this case, $\beta$-ET$_2$I$_3$ has only an inversion symmetry, whereas $\beta'$-EtMe$_3$P[Pd(dmit)$_2$]$_2$ contains one distinct cation and one Pd(dmit)$_2$ monomer, from which the other member of the dimer is derived by inversion symmetry, and two distinct cations. The Pd(dmit)$_2$ dimers are related by an inversion symmetry within layers and by a screw rotation symmetry in alternating layers. Images rendered in Mercury.[23]
The trick to solving the infinite lattice systems is to take the Fourier transform of the system, resulting in an expression of the Hamiltonian in momentum space. The Fourier transform of the annihilation operator is

$$\hat{c}_{i\sigma} = \sum_k \langle i|k \rangle \hat{c}_{k\sigma} = \frac{1}{\sqrt{N}} \sum_k e^{ik \cdot r_i} \hat{c}_{k\sigma} \quad \text{(2.5)}$$

where $N$ is the number of sites, and the Fourier transform of the conjugate creation operator is

$$\hat{c}_{i\sigma}^\dagger = \sum_k \langle k|i \rangle \hat{c}_{k\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot r_i} \hat{c}_{k\sigma}^\dagger \quad \text{(2.6)}$$

Substituting (2.5) and (2.6) into the Hamiltonian produces

$$\hat{H} = \frac{\mu}{N} \sum_{i\sigma} \sum_{k\k'} e^{ik \cdot r_i} e^{-ik' \cdot r_i} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma} - \frac{t}{N} \sum_{i\sigma} \sum_{k\k'} \sum_{\sigma} e^{ik \cdot r_i} e^{-ik' \cdot r_i} e^{-ik' \cdot a} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma}$$

$$+ e^{ik' \cdot r_i} e^{-ik' \cdot a} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma}$$

$$= \frac{\mu}{N} \sum_{k\k'} \sum_{i\sigma} e^{i(k' - k) \cdot r_i} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma}^\dagger - \frac{t}{N} \sum_{k\k'} \sum_{i\sigma} e^{i(k' - k) \cdot r_i} e^{-ik' \cdot a} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma}$$

$$+ e^{i(k' - k) \cdot r_i} e^{-ik' \cdot a} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma}$$

Using the identity

$$\sum_i e^{i(k - k') \cdot r_i} = N \delta(k - k') \quad \text{(2.8)}$$

we may remove the sum over $k'$. 
2.2 The tight-binding model

Figure 2.6: The tight-binding model in one dimension produces a simple dispersion relation \( E = \mu - 2t \cos(k_a) \). The Fermi surface is the \( N - 1 \) dimensional surface of \( E = \mu \). For the one dimensional case, this is simply two points, or one if \( \mu \) corresponds to the bottom or top of the band.

\[
\begin{align*}
\hat{H} &= \frac{\mu}{N} \sum_{k_\sigma} \hat{c}_{k_\sigma}^\dagger \hat{c}_{k_\sigma} - \frac{t}{N} \sum_{k_\sigma} e^{-ik_a} \hat{c}_{k_\sigma}^\dagger \hat{c}_{k_\sigma} \\
&\quad + e^{ik_a} \hat{c}_{k_\sigma}^\dagger \hat{c}_{k_\sigma} \\
&= \mu \sum_{k_\sigma} \hat{n}_{k_\sigma} - t \sum_{k_\sigma} (e^{ik_a} + e^{-ik_a}) \hat{n}_{k_\sigma} \\
&= \sum_{k_\sigma} (\mu - 2t \cos(k \cdot a)) \hat{n}_{k_\sigma},
\end{align*}
\]

where \( \hat{n}_{k_\sigma} = \hat{c}_{k_\sigma}^\dagger \hat{c}_{k_\sigma} \) is the particle number operator for the state defined by momentum \( k \) and spin \( \sigma \). Setting arbitrary values for the parameters, the solution can be plotted over the first Brillouin zone (see Figure (2.6)).
2.2.2 2D lattices — square and triangular

The ET and Pd(dmit)$_2$ based materials studied in this work have a quasi-2D layered crystal structure. Therefore, a tight-binding model of these materials would contain in-plane hopping terms (e.g. $t, t'$) and interlayer hopping terms, $t_\perp$. However, $t_\perp << t$ and interlayer hopping terms play a minor role in the low energy effective Hamiltonian. Therefore, these materials can be represented in a minimal model by 2D lattices.

Understanding the tight-binding model on 2D lattices is easiest in simple, highly symmetric cases such as the square lattice. Then, the square lattice is compared to the isotropic and then anisotropic triangular lattices, which is the lattice that represents the geometric arrangement of the ET or Pd(dmit)$_2$ units within the crystal.

Square lattice

The square lattice is essentially an extension of the linear chain into two dimensions. The Hamiltonian for this is:

$$\hat{H} = \mu \sum_{ij} \hat{c}_{ij\sigma}^\dagger \hat{c}_{ij\sigma} - t \sum_{ij\sigma} \hat{c}_{ij\sigma} \hat{c}_{i+1j\sigma} + \hat{c}_{i+1j\sigma}^\dagger \hat{c}_{ij\sigma} + \hat{c}_{ij\sigma}^\dagger \hat{c}_{i+1\sigma} + \hat{c}_{i+1\sigma}^\dagger \hat{c}_{ij\sigma} \quad (2.10)$$

Lattice sites are now labelled by two indices, $i$ and $j$. Here, they denote position within the lattice. For example, if the lattice were in the $x - y$ plane, site $(i+1, j)$ would be the nearest neighbour to site $(i, j)$ in the $+x$ direction. There are four possible nearest-neighbour hops, each defined here with the same hopping coefficient $t$. The lattice spacing is again $a$, in both directions.

Transforming the operators into momentum space gives:

$$\hat{c}_{ij\sigma} = \frac{1}{\sqrt{N}} \sum_{ijk} \langle ij | k \rangle \hat{c}_{k\sigma} = \frac{1}{\sqrt{N}} \sum_{ijk} e^{ik \cdot r_{ij}} \hat{c}_{k\sigma} \quad (2.11)$$

and the conjugate creation operator yields:
2.2 The tight-binding model

\[
\hat{c}_{ij\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_{ijk} (k|ij) \hat{c}_{k\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_{ijk} e^{-ik\cdot r_{ij}} \hat{c}_{k\sigma}^\dagger
\]  

(2.12)

The vectors for neighbouring lattice sites are

\[
\begin{align*}
    r_{i+1j} &= r_{ij} + a \hat{e}_i = r_{ij} + \hat{a} i \\
    r_{ij+1} &= r_{ij} + a \hat{e}_j = r_{ij} + \hat{a} j
\end{align*}
\]

(2.13)

Substituting these back into the Hamiltonian gives

\[
\hat{H} = \frac{\mu}{N} \sum_{kk'} \sum_{ij\sigma} e^{i(k-k')\cdot r_{ij}} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma} - \frac{t}{N} \sum_{kk'} \sum_{ij\sigma} e^{i(k-k')\cdot r_{ij}} e^{i\frac{a x}{2}} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma} + e^{i(k-k')\cdot r_{ij}} e^{-i\frac{a y}{2}} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma} + e^{i(k-k')\cdot r_{ij}} e^{i\frac{a x}{2}} e^{-i\frac{a y}{2}} \hat{c}_{k\sigma}^\dagger \hat{c}_{k'\sigma} \\
\end{align*}
\]

= \frac{\mu}{N} \sum_{k\sigma} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} - \frac{t}{N} \sum_{k\sigma} e^{ika} + e^{-ika} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + e^{ika} + e^{-ika} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} \\
\end{align*}
\]

= \sum_{k\sigma} [\mu + \epsilon(k)] \hat{\Pi}_{k\sigma}
\]

(2.14)

Since the Hamiltonian is diagonalised in \( \mathbf{k} \), the dispersion relation \( \epsilon(k) \) can be read directly from the result. The relation is shown in Figure (2.7), again for conveniently selected values of \( \mu, a \) and \( t \). The plot shows more than the first Brillouin zone, to illustrate the periodicity of the dispersion relation.

**Isotropic triangular lattice**

The isotropic triangular lattice is solved in a manner very similar to the square lattice, except this time the lattice basis vectors are defined as \( \hat{e}_i = \hat{\imath} \) and \( \hat{e}_j = \frac{1}{2} \hat{\imath} + \frac{\sqrt{3}}{2} \hat{j} \).
Figure 2.7: The dispersion relation (left) of the tight-binding model on a square lattice produces the marginally more complicated two dimensional analog of the one dimensional tight-binding model. In this simple case, the FBZ (right) is bounded by a square with corners at the four peaks shown. The Fermi surface is the contour plot of the dispersion relation at \( E = \mu \). \( \mu = 0 \), \( t = 1 \), and \( a = 1 \), in arbitrary units. The filling of the system can be measured by calculating the area of the FBZ enclosed by the Fermi surface. \( \mu = 0 \) (green diamond) corresponds to half-filling in this case.

There are six available neighbours to each lattice site, located (relative to \( r_{ij} \)) at \( r_{i+1j} \), \( r_{i-1j} \), \( r_{ij+1} \), \( r_{ij-1} \), \( r_{i+1j-1} \), and \( r_{i-1j+1} \). The Hamiltonian is

\[
\hat{H} = \mu \sum_{ij\sigma} \hat{c}_{ij\sigma}^\dagger \hat{c}_{ij\sigma} - t \sum_{ij\sigma} \left( \hat{c}_{ij\sigma}^\dagger \hat{c}_{i+1j\sigma} + \hat{c}_{i-1j\sigma}^\dagger \hat{c}_{ij+1\sigma} + \hat{c}_{ij+1\sigma}^\dagger \hat{c}_{ij-1\sigma} + \hat{c}_{ij-1\sigma}^\dagger \hat{c}_{i+1j\sigma} + \hat{c}_{ij\sigma}^\dagger \hat{c}_{i+1j-1\sigma} + \hat{c}_{i+1j-1\sigma}^\dagger \hat{c}_{ij\sigma} \right).
\]

(2.15)

By transforming to momentum space and applying the same method as used in the square lattice, the Hamiltonian becomes

\[
\hat{H} = \frac{\mu}{N} \sum_{k\sigma} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} - t \sum_{k\sigma} \left( e^{i(k_x a)} + e^{-i(k_x a)} \right) \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma}
\]

\[
+ \left( e^{i\left(\frac{a\sqrt{3}}{2} k_y + \frac{a\sqrt{3}}{2} k_y\right)} + e^{-i\left(\frac{a\sqrt{3}}{2} k_x + \frac{a\sqrt{3}}{2} k_y\right)} \right) \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + \left( e^{i\left(\frac{a\sqrt{3}}{2} k_x - \frac{a\sqrt{3}}{2} k_y\right)} + e^{-i\left(\frac{a\sqrt{3}}{2} k_x - \frac{a\sqrt{3}}{2} k_y\right)} \right) \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma}
\]

\[
= \sum_{k\sigma} \mu - 2t \left( \cos(k_x a) + \cos\left(\frac{a}{2} k_x + \frac{a\sqrt{3}}{2} k_y\right) + \cos\left(\frac{a}{2} k_x - \frac{a\sqrt{3}}{2} k_y\right) \right) \hat{n}_{k\sigma}.
\]

(2.16)
2.2 The tight-binding model

The tight-binding model on an isotropic triangular lattice produces a marginally more complicated dispersion (left) and Fermi surface (right) compared to the tight-binding dispersion on a square lattice. The dispersion relation has been extended out past the boundary of the First Brillouin Zone, a hexagonal shape in the case, marked by the thick black line. The anisotropic triangular lattice differs from the isotropic case in two ways. Anisotropy in the lattice parameters (i.e. $a$ $b$) will produce a commensurate distortion in the shape of the FBZ and the dispersion relation. Anisotropy in the values of $t$ will result in different widths of the band in different directions, changing the relative height of the peaks at the FBZ boundary. $\mu = 0$, $t = 1$, and $a = 1$, in arbitrary units.

Using the trigonometric identity $\cos(x + y) + \cos(x - y) = 2\cos(x)\cos(y)$

The solution becomes

$$\hat{H} = \sum_{k\sigma}(\mu - 2t\cos(k_xa) - 4t\cos(\frac{a}{2}k_x)\cos(\frac{a\sqrt{3}}{2}k_y))\hat{n}_{k\sigma}. \quad (2.17)$$

The dispersion relation is shown in Figure (2.8).

Anisotropic triangular lattice

This is the lattice type that directly relates to the ET and Pd(dmit)$_2$ crystal structures. By considering dimers of the molecular unit as lattice sites, the crystal takes on the geometry of the anisotropic triangular lattice (see Figure (2.4)).

The anisotropic triangular lattice solution is very similar to that of the isotropic triangular lattice. The only difference is that two of the six neighbours have a hopping integral $t'$
instead of \( t \). Setting the co-ordinate system such that the \( t' \) hops occur along the x-axis, the Hamiltonian is:

\[
\hat{\mathcal{H}} = \mu \sum_{ij\sigma} \hat{c}_{ij\sigma}^{\dagger} \hat{c}_{ij\sigma} - t' \sum_{ij\sigma} \hat{c}_{ij\sigma}^{\dagger} \hat{c}_{i+1j\sigma} + \hat{c}_{i+1j\sigma}^{\dagger} \hat{c}_{ij\sigma} \\
-t \sum_{ij\sigma} \hat{c}_{ij\sigma}^{\dagger} \hat{c}_{ij+1\sigma} + \hat{c}_{ij+1\sigma}^{\dagger} \hat{c}_{ij\sigma} + \hat{c}_{ij\sigma}^{\dagger} \hat{c}_{i+1j-1\sigma} + \hat{c}_{i+1j-1\sigma}^{\dagger} \hat{c}_{ij\sigma}
\] (2.18)

Assuming the hops along \( t \) directions make an angle of 45° from the x axis, then the lattice spacing is \( a \) along \( t' \) hops and \( \frac{a}{\sqrt{2}} \) along \( t \) hops. The two basis vectors are

\[
\hat{e}_i = a \hat{i} \\
\hat{e}_j = \frac{a}{2} \hat{i} + \frac{a}{2} \hat{j}
\] (2.19)

By the same method as above, the Hamiltonian becomes:

\[
\hat{\mathcal{H}} = \sum_{k\sigma} \mu - (2t' \cos(k_xa) - 4t \cos(\frac{a}{2}k_x) \cos(\frac{a}{2}k_y)) \hat{n}_{k\sigma}
\] (2.20)

The dispersion relation is very similar to that of the isotropic triangular lattice, except for the shape of the FBZ and the relative position of the dispersion peaks.

### 2.3 The Hubbard model

As effective as the tight-binding model is at describing the electronic properties of simple crystalline materials, the lack of any treatment of electron-electron interactions means this model cannot capture the physics of materials in which these interactions are significant, i.e. strongly-correlated materials.

Hubbard[24] proposed a way of introducing electron-electron interactions in a partial way, by including a Coulomb repulsion term that only considers electrons localised on the same lattice site, or in the case of extended Hubbard models, nearby lattice sites as well.
The Hamiltonian for the Hubbard model is

\[ \hat{H} = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - t \sum_{ij\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c. \]  

(2.21)

where \( U \) is the Coulomb energy associated with two electrons on the same lattice site and \( i \) and \( j \) are neighbouring lattice sites, as with the tight-binding model.

### 2.3.1 One site solution and the atomic limit

It is trivial to solve the single site Hubbard model; one finds that

\[
\begin{align*}
E_1 &= E_0 + \epsilon \\
E_2 &= E_0 + 2\epsilon + U
\end{align*}
\]

(2.22a)  (2.22b)

where \( E_n \) is the energy of the model with \( n \) electrons. It follow immediately from (2.22) that

\[
U = E_0 + E_2 - 2E_1. 
\]

(2.23)

It is clear from Eq. (2.22) that the site energy is given by

\[
\epsilon = E_1 - E_0. 
\]

(2.24)

One can also write Eq. (2.21) in terms of the hole operators defined by \( \hat{h}_{i\sigma}^\dagger \equiv \hat{c}_{i\sigma} \) which gives

\[
\hat{H}_i = E_2 + \xi_m \hat{h}_{i\sigma}^\dagger \hat{h}_{i\sigma} + U \hat{h}_{i\uparrow}^\dagger \hat{h}_{i\uparrow} \hat{h}_{i\downarrow}^\dagger \hat{h}_{i\downarrow},
\]

(2.25)

where,

\[
\xi = -(\epsilon + U) = E_1 - E_2
\]

(2.26)

is the site energy for holes. Physically \( \epsilon \) and \( \xi \) correspond to the electron affinity and ionisation energy, respectively. Thus one sees that while the Hubbard \( U \) is the same for
Background theory

Figure 2.9: Schematic of the Hubbard models studied for the ET salts. The left panel shows the two site extended Hubbard model. Here each site represents a monomer. The Coulomb interactions ($U_m$ between electrons on the same monomer and $V_m$ between electrons on different monomers) and the hopping integral, $t$, are marked. The right panel shows the dimerised model. As the bonding orbital is filled only a single state is relevant, thus the only parameter is the effective Coulomb repulsion between electrons/holes in that state, $U_d$. This model does not extend to the Pd(dmit)$_2$ materials, where the interactions of other monomer orbitals must be accounted for.

electrons and holes, the site energy is not.

2.3.2 Two site solution

A two site extended Hubbard model is useful for considering intradimer dynamics.[7]

$$\hat{\mathcal{H}} = \sum_{i\sigma} \xi_{mi} \hat{n}_{i\sigma} - t \sum_{\sigma} (\hat{h}_{1\sigma}^\dagger \hat{h}_{2\sigma} + h.c.) + \sum_i U_{mi} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + V_m \hat{n}_1 \hat{n}_2$$

(2.27)

where $\hat{h}_{i\sigma}^{(\dagger)}$ annihilates (creates) a hole on site (monomer) $i$ in spin state $\sigma$, $\xi_{mi}$ is the site energy for holes on site $i$, $\hat{n}_{i\sigma}$ is the number operator for spin $\sigma$ holes on site $i$, $\hat{n}_i = \sum_{\sigma} \hat{n}_{i\sigma}$, $t$ is the inter-monomer hopping integral, $U_{mi}$ is the effective on-site (monomer) Coulomb repulsion, and $V_m$ is the intersite Coulomb repulsion.
The lowest energy eigenvalues of Hamiltonian (2.27) for each charge state are

\[ E(0) = 0, \]  
\[ E(1) = \xi_m - \frac{1}{2} \sqrt{4t^2 + (\Delta \xi_m)^2}, \]  
\[ E(2) = 2\xi_m + \frac{1}{3} \left( 2U_m + V_m - 2A \cos \theta \right), \]

where \( \xi_m = \frac{1}{2}(\xi_{m1} + \xi_{m2}), A = 12t^2 + (\Delta U_m)^2 + (U_{m1} - V_m)(U_{m2} - V_m) + 3(\Delta \xi_m)^2, \)
\[ \cos 3\theta = \frac{(U_m - 2V_m)[18t^2 - (2U_{m1} - U_{m2} - V_m)(U_{m1} - 2U_{m2} + V_m) - 9(\Delta \xi_m)^2]/2A^3. \]
\[ \Delta \xi_m = \xi_{m1} - \xi_{m2}, \]
\[ \overline{U}_m = \frac{1}{2}(U_{m1} + U_{m2}), \] and \( \Delta U_m = U_{m1} - U_{m2}. \)

The case of two monomers with different site energies and on-site Coulomb repulsion may be solved by a general method for diagonalising cubic matrix eigensystems.\[25\] In physical systems, cases where the two monomers within a dimer have the same geometry (e.g., by symmetry), \( \xi_{m1} = \xi_{m2} = \xi_m \) and \( U_{m1} = U_{m2} = U_m \) and the eigenvalues simplify to

\[ E(1) = \xi_m - t \]  
\[ E(2) = 2\xi_m + \frac{1}{2} \left( U_m + V_m - \sqrt{16t^2 + (U_m - V_m)^2} \right), \]

in which case the solution is straightforward.

In the limit \( U_m = V_m = 0 \) the two site Hubbard model has two solutions: the bonding state \( |\phi_{\sigma} \rangle = |\phi_{1\sigma} \rangle + |\phi_{2\sigma} \rangle \) and the antibonding state \( |\phi_{\sigma} \rangle = |\phi_{1\sigma} \rangle - |\phi_{2\sigma} \rangle \), where \( |\phi_{i\sigma} \rangle = \hat{h}_{i\sigma} |0 \rangle \) is a single hole state centred on the \( i^{th} \) monomer and \( |0 \rangle \) is the (particle) vacuum state.

### 2.3.3 Perturbation theory

It is also instructive to solve the two site Hubbard model using time-independent perturbation theory. In this theory, it is assumed that the Hamiltonian may be partitioned into a dominant term and a perturbation term.
\[ \hat{H} = \hat{H}_0 + \hat{H}_P. \] (2.30)

In the case of the Hubbard model for \( U \gg t \), the Coulomb terms would be the dominant \( \hat{H}_0 \) part and the hopping terms would be the weaker \( \hat{H}_P \) part. The solution of this Hamiltonian may then be found by approximating the eigenstates of the system to zero order with the eigenstates of \( \hat{H}_0 \), and applying a successive approximation to the eigenvalues and eigenstates by means of an algebraic series.

In second-quantised notation, the basis set for the two site, two particle system is

\[ \left| 1 \uparrow 1 \downarrow \rightangle , \left| 1 \uparrow 2 \uparrow \rightangle , \left| 1 \uparrow 2 \downarrow \rightangle , \left| 1 \downarrow 2 \uparrow \rightangle , \left| 1 \downarrow 2 \downarrow \rightangle , \left| 2 \uparrow 2 \downarrow \rightangle \] (2.31)

where \( \left| n \sigma \right\rangle = \hat{c}_{n\sigma}^\dagger \left| 0 \right\rangle \), and \( \left| 0 \right\rangle \) is a vacuum state. The corresponding energy eigenvalues of these states from \( \hat{H}_0 \) are \( U, 0, 0, 0, 0, \) and \( U \), respectively.

First-order corrections to the eigenvalues of the system are calculated by finding the matrix elements of each state in the basis from \( \hat{H}_P \), i.e.

\[ E_1(n) = \sum_m \langle m | \hat{H}_P | m \rangle. \] (2.32)

However, since the diagonal elements of \( \hat{H}_P \) in matrix form are zero, the sum is zero and there is no first-order energy correction.

The second-order energy corrections involve applying an extra sum over the basis functions, again applied to \( \hat{H}_P \)

\[ E_2(n) = \sum_{m \neq n} \frac{|\langle m | \hat{H}_P | n \rangle|^2}{E_n - E_m} \] (2.33)

where \( E_n \) and \( E_m \) are the energies of the states \( (n, m) \) in \( \hat{H}_0 \).

The only state pairs \( (n, m) \) for which the matrix elements on the numerator are nonzero are those which describe the ‘hopping’ of one particle from one site to the other. This leads to two constraints on the combinations of states. First, the particles must have opposite spin. Therefore, the states \( |1\uparrow 2\uparrow \rangle \) and \( |1\downarrow 2\downarrow \rangle \) have no second-order energy correction. The
second condition is that nonzero state pairs \((n, m)\) must be such that one of the states has both particles on the same site and the other state has one particle on each site. The four remaining states each have nonzero matrix elements with both states of the other charge distribution. For example, the state \(|1\uparrow 1\downarrow\rangle\) is connected to the states \(|1\uparrow 2\downarrow\rangle\) and \(|1\downarrow 2\uparrow\rangle\) with amplitude \(|t|\). Therefore, the second-order energy corrections for these states with opposite spin are \(\frac{2t^2}{U}\) for the states with both particles on one site and \(-\frac{2t^2}{U}\) for the states with one particle per site. This splitting of the energy levels between these two types of state implies that the lower energy (more distributed) states are the dominant contribution to the true ground state of the system. In the low temperature regime, \(k_BT << \frac{t^2}{U}\), the higher energy localised states would be frozen out of the ground state completely.

### 2.3.4 Infinite crystal solutions

Of course, the application of the Hubbard model to full crystals would be an excellent test of the model’s effectiveness. However, there is a major problem with this. The \(U\) term of the Hubbard model characterises a site-localised phenomenon naturally described in a localised real space basis, whereas the \(t\) terms characterise motion through the crystal lattice, naturally described in a \(k\)-space basis (like in the tight-binding model). Therefore, an exact solution of the model in infinite crystals would require finding eigenstates that are diagonalisable in both real and \(k\)-space. However, the general solution is only known for one and infinite dimensions. Even if such a solution were found, the sheer enormity of such quantum many-body systems would make finding a solution computationally intractable.

The one dimensional Hubbard model does in fact have an exact solution, due to an application of the Bethe ansatz[26]. The Bethe ansatz reduces the interactions in the quantum many-body system to a product of two-body interactions. Effectively, a many-body interaction is equivalent to a combination of two-body interactions. The Bethe ansatz was originally applied to the one dimensional Heisenberg model, but has been shown to work for other one dimensional models. Two examples are the Hubbard model[27, 28] and the Anderson model[29, 30], which resembles the Hubbard model but particle interactions only occur on particular ‘impurity’ sites.
This method for solving the one dimensional Hubbard model does not apply to other cases which we shall consider, so I direct the interested reader to Essler’s highly detailed monograph on the subject.[31]

The solution to the one dimensional Hubbard model can apply to the extreme scenario of the anisotropic triangular lattice in which $t = 0$, producing a series of uncoupled linear chains. In other two dimensional regimes, the problem of finding analytical solution remains.

Approximate solutions may be found, for example, from renormalisation group methods (RG)[32] and dynamical mean-field theory (DMFT)[33], which is exact in infinite dimensions.

### 2.4 Density functional theory

A comprehensive treatise on density functional theory (DFT) would easily consume more space than is afforded here. Therefore, I direct the interested reader to Jones and Gunnarsson’s excellent review article[34] or some very accessible textbooks.[35, 36] In this section, I shall introduce the fundamentals of the theory, a few of the variety of approximation schemes used to simplify or speed the associated calculations, and the computational implementations of the theory used to study ET and Pd(dmit)$_2$ materials, as well as simpler materials used for testing and benchmarking the computer code.

DFT is concerned with the solution to the many-body time independent Schrödinger equation

$$\hat{H}|\psi(x_1, x_2, \ldots, x_n)\rangle = \hat{H}|\psi(\{x_i\})\rangle = E|\psi(\{x_i\})\rangle.$$ (2.34)

In its application to the fields of chemistry and condensed matter physics, the state $\psi(\{x_i\})$ usually describes a system of $M$ nuclei and $N$ electrons. The parameter space in which the state is defined here consists of position ($r_n$ for electrons and $R_m$ for nuclei), nuclear charge, $Z_m$, and electron spin state, $\sigma_n$.

$$\psi(\{x_i\}) = \psi(\{r_n, \sigma_n\}, \{R_m, Z_m\})$$ (2.35)

One may also include a nuclear spin representation, but this rarely has any effect on quantum chemistry or condensed matter physics applications. The Hamiltonian ($\hat{H}$) for these
systems consists of a single-particle kinetic energy $\hat{T}$, a single-particle ‘external’ potential $\hat{V}$, and two-particle Coulomb interactions $\hat{W}$.

\[
\hat{H} = \hat{T} + \hat{W} + \hat{V}
\]  \hspace{1cm} (2.36)

where

\[
\hat{T} = -\frac{1}{2m_e} \sum_{n=1}^{N} \nabla_n^2 - \frac{1}{2} \sum_{m=1}^{M} \frac{1}{m_m} \nabla_m^2
\]

\[
\hat{W} = \frac{1}{2} \sum_{i \neq n} \frac{1}{|r_i - r_n|} + \frac{1}{2} \sum_{n=1}^{N} \sum_{m=1}^{M} \frac{Z_m}{|r_n - R_m|} + \sum_{j \neq m} \frac{Z_j Z_m}{|R_j - R_m|}
\]

\[
\hat{V} = \sum_{n=1}^{N} V_e(r_n, \sigma_n) + \sum_{m=1}^{M} V_n(R_m, Z_m).
\]  \hspace{1cm} (2.37)

$\nabla_n$ and $\nabla_m$ are single-particle gradient operators that act only on that part of the many-body wavefunction defined in the space $r_n$ and $R_m$ respectively, $m_e$ is the mass of an electron, and $m_m$ is the mass of the $m^{th}$ nucleus. $\hat{V}$ has been left with an abstract definition for the moment, and represents the potential energy of the electrons and nuclei that is not due to electrostatic interactions between these particles. These equations are in ‘natural’ units, i.e. $|e| = \hbar = \frac{1}{4\pi \epsilon_0} = 1$.

### 2.4.1 The Born-Oppenheimer Approximation

Solving the Hamiltonian (2.36) outright is a highly nontrivial task. Several approximations, assumptions and constraints may be applied to make the problem tractable. One such simplification is the Born-Oppenheimer approximation.[37] Consider the kinetic energy term in the Hamiltonian for a molecular system

\[
\hat{T} = -\frac{1}{2m_e} \sum_{n=1}^{N} \nabla_n^2 - \frac{1}{2} \sum_{m=1}^{M} \frac{1}{m_m} \nabla_m^2.
\]  \hspace{1cm} (2.38)

The mass of the lightest nucleus, hydrogen, is approximately 1800 times the mass of
an electron. Therefore, the dynamics of the electrons take place on a much shorter time scale than the dynamics of the nuclei in most situations. In anticipation of the iterative numerical technique for solving the ground state of the entire system, it is a very good approximation to partition the system wavefunction into separate many-body nuclear and electronic wavefunctions.

\[ \psi(\{r_n, \sigma_n\}, \{R_m, Z_m\}) \approx \psi_e(\{r_n, \sigma_n\})\psi_n(\{R_m, Z_m\}). \quad (2.39) \]

This is the Born-Oppenheimer approximation. Once this approximation is made, the solution of (2.36) becomes much simpler. During each iteration of the solution process, the nuclear wavefunction \( \psi_n(\{R_m, Z_m\}) \) is assumed to be constant, while the electronic wavefunction \( \psi_e(\{r_n, \sigma_n\}) \) is solved. Then the nuclear wavefunction is ‘relaxed’ towards its minimum energy configuration, and the next iteration begins. The process is repeated until the nuclear wavefunction converges.

As a result of this, the second term in \( \hat{T} \) may be ignored during the solution of the electronic wavefunction. Furthermore, \( \hat{W} \) is greatly simplified:

\[
\hat{W} = \frac{1}{2} \sum_{i \neq n} \frac{1}{|r_i - r_n|} + \frac{1}{2} \sum_{n=1}^{N} \sum_{m=1}^{M} \frac{Z_m}{|r_n - R_m|} \\
+ \frac{1}{2} \sum_{j \neq m} \frac{Z_j Z_m}{|R_j - R_m|} \\
= \hat{W}_{ee} + \hat{W}_{en} + \hat{W}_{nn} \quad (2.40)
\]

where each term has been labelled according to the particles that participate in each interaction (\( e \) for electrons and \( n \) for nuclei). \( \hat{W}_{ee} \) remains unchanged, because it is purely an electron-electron interaction. \( \hat{W}_{en} \) however undergoes a fundamental change to its form. Instead of a two-particle interaction between each electron and each nucleus, it may now be considered a single-particle potential experienced by each electron, due to the nuclear wavefunction.
\[ \hat{W}_{\text{en}}(\mathbf{r}) = \sum_{m=1}^{M} \frac{Z_m}{|\mathbf{r} - \mathbf{R}_m|} = \hat{V}(\mathbf{r}) \]  

(2.41)

In the absence of any other external potential on the system, \( \hat{V}(\mathbf{r}) \) becomes the external potential on the electronic wavefunction.

\( \hat{W}_{\text{nn}} \) is the two-body nucleus-nucleus interaction. If the nuclear wavefunction is held constant, then this term is also constant and may be ignored when deriving the calculation of the electronic wavefunction. It is still used when solving for the lowest energy nuclear configuration (relaxation).

Putting these results together, the Hamiltonian for the electronic wavefunction of the system still retains the form \( \hat{H} = \hat{T} + \hat{W} + \hat{V} \), except now the components are much simpler

\[ \begin{align*}
\hat{T} &= -\frac{1}{2} \sum_{n=1}^{N} \nabla^2_n \\
\hat{W} &= \frac{1}{2} \sum_{i \neq n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_n|} \\
\hat{V} &= \sum_{n=1}^{N} V(\mathbf{r}_n) \\
V(\mathbf{r}) &= \sum_{m=1}^{M} \frac{Z_m}{|\mathbf{r} - \mathbf{R}_m|}. 
\end{align*} \]  

(2.42)

The Born-Oppenheimer approximation greatly reduces the complexity of this many-body system. It is a separate part from DFT, having a larger scope of application, but the two are typically used in conjunction. However, the Hamiltonian in this current form is still far from computationally tractable for all but the simplest systems. The next simplification is the most definitive element of DFT: the Hohenberg-Kohn theorem.

### 2.4.2 The Hohenberg-Kohn Theorem

The Hohenberg-Kohn Theorem will allow us to replace the many-body electronic wavefunction \( \psi(\{\mathbf{r}_n, \sigma_n\}) \) in these calculations with a density function
\[ \rho(r_1) = \int d^3r_2 d^3r_3 \ldots d^3r_N \psi^*({\{r_i, \sigma_i\}})\psi({\{r_i, \sigma_i\}}) \] (2.43)

such that the ground state energy \( E_0 \) of a system may be found from a functional of \( \rho(r) \), rather than directly solving the Schrödinger equation. I.e. instead of solving

\[ \hat{H}\psi({\{r_i, \sigma_i\}}) = E\psi({\{r_i, \sigma_i\}}) \] (2.44)

we shall solve

\[ H[\rho(r)] = E_0 \] (2.45)

where \( H[\rho(r)] \) denotes a functional \( H \) acting on the ground state density function \( \rho(r) \).

A functional is conceptually similar to a function. Whereas a function \( f(x) \) takes scalar values \( x \) as input, and returns a scalar output (e.g., \( y = f(x) = x^2 \)), a functional \( A[f(x)] \) takes a function as input and returns a scalar output, e.g.

\[ A[f(x)] = \int_{-\infty}^{\infty} dx f(x). \]

It is important to stress the point that (2.45) returns the ground state energy, \( E_0 \), whereas (2.44) is valid for all eigenstates of the system.

In order for this to be valid, there must be a 1:1 mapping between any particular Hamiltonian and its associated ground state density. The Hohenberg-Kohn theorem is simply the proof that this is the case. Recalling the Hamiltonian for a many-body electronic wavefunction in the presence of nuclei

\[ \hat{H} = \hat{T} + \hat{W} + \hat{V} \]

\[ = -\frac{1}{2} \sum_{n=1}^{N} \nabla^2 n + \frac{1}{2} \sum_{i \neq n} \frac{1}{|r_i - r_n|} + \sum_{n=1}^{N} V(r_n), \]

the external potential \( \hat{V} \) uniquely defines the system. For any particular \( \hat{V} \), define \( \hat{H}_V \), \( E_V, \psi_V({\{r_i, \sigma_i\}}) \) and \( \rho_V(r) \) as the relevant Hamiltonian, ground state energy, ground state
2.4 Density functional theory

electronic wavefunction and ground state electron density function, respectively. Hence

\[ \hat{H}_V |\psi_V(\{r_i, \sigma_i\})\rangle = E_V |\psi_V(\{r_i, \sigma_i\})\rangle. \]  

(2.46)

Consider two different potentials \( \hat{V} \) and \( \hat{V}' \). The expectations of the associated Hamiltonians will be a minimum when operated on the associated ground state wavefunctions, which are assumed to be non-degenerate. Therefore

\[
\langle \psi_V(\{r_i, \sigma_i\}) | \hat{H}_V | \psi_V(\{r_i, \sigma_i\}) \rangle < \langle \psi_{V'}(\{r_i, \sigma_i\}) | \hat{H}_V | \psi_{V'}(\{r_i, \sigma_i\}) \rangle \]  

(2.47)

\[
\langle \psi_{V'}(\{r_i, \sigma_i\}) | \hat{H}_V | \psi_{V'}(\{r_i, \sigma_i\}) \rangle < \langle \psi_V(\{r_i, \sigma_i\}) | \hat{H}_V | \psi_V(\{r_i, \sigma_i\}) \rangle. \]  

(2.48)

Partitioning the Hamiltonian and separating the system-independent part \((\hat{T} + \hat{W})\) from the system-dependent part \((\hat{V})\) yields

\[
\langle \psi_V(\{r_i, \sigma_i\}) | \hat{H}_V | \psi_V(\{r_i, \sigma_i\}) \rangle = \langle \psi_V(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} + \hat{V} | \psi_V(\{r_i, \sigma_i\}) \rangle = \langle \psi_V(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} | \psi_V(\{r_i, \sigma_i\}) \rangle + \langle \psi_V(\{r_i, \sigma_i\}) | \hat{V} | \psi_V(\{r_i, \sigma_i\}) \rangle
\]

Substituting this back into (2.47) and (2.48) and adding the two equations yields

\[
\langle \psi_V(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} | \psi_V(\{r_i, \sigma_i\}) \rangle + \langle \psi_V(\{r_i, \sigma_i\}) | \hat{V} | \psi_V(\{r_i, \sigma_i\}) \rangle + \langle \psi_{V'}(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} | \psi_{V'}(\{r_i, \sigma_i\}) \rangle + \langle \psi_{V'}(\{r_i, \sigma_i\}) | \hat{V} | \psi_{V'}(\{r_i, \sigma_i\}) \rangle < \langle \psi_V(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} + \hat{V} | \psi_V(\{r_i, \sigma_i\}) \rangle + \langle \psi_{V'}(\{r_i, \sigma_i\}) | \hat{T} + \hat{W} + \hat{V} | \psi_{V'}(\{r_i, \sigma_i\}) \rangle
\]
\[
\begin{aligned}
&\langle \psi_V'(\{r_i, \sigma_i\})|\hat{T} + \hat{W} | \psi_V'(\{r_i, \sigma_i\}) \rangle + \langle \psi_V'(\{r_i, \sigma_i\})|\hat{V} | \psi_V'(\{r_i, \sigma_i\}) \rangle \\
&- \left( \langle \psi_V'(\{r_i, \sigma_i\})|\hat{T} + \hat{W} | \psi_V'(\{r_i, \sigma_i\}) \rangle + \langle \psi_V'(\{r_i, \sigma_i\})|\hat{V} | \psi_V'(\{r_i, \sigma_i\}) \rangle \right)
\end{aligned}
\]

\[
\begin{aligned}
&\langle \psi_V'(\{r_i, \sigma_i\})|\hat{T} + \hat{W} | \psi_V'(\{r_i, \sigma_i\}) \rangle + \langle \psi_V'(\{r_i, \sigma_i\})|\hat{V} | \psi_V'(\{r_i, \sigma_i\}) \rangle \\
&- \left( \langle \psi_V'(\{r_i, \sigma_i\})|\hat{T} + \hat{W} | \psi_V'(\{r_i, \sigma_i\}) \rangle + \langle \psi_V'(\{r_i, \sigma_i\})|\hat{V} | \psi_V'(\{r_i, \sigma_i\}) \rangle \right)
\end{aligned}
\]

\begin{equation}
(2.49)
\end{equation}

Converting the Dirac notation into integral notation

\[
\langle \psi_V'(\{r_i, \sigma_i\})|\hat{V} | \psi_V'(\{r_i, \sigma_i\}) \rangle = \int d^3 r_1 d^3 r_2 \ldots d^3 r_n \psi_V^*(\{r_i, \sigma_i\}) \hat{V} \psi_V(\{r_i, \sigma_i\})
\]

and noting that the external potential \(\hat{V} = V(r)\) is a single-particle function that commutes with the electronic wavefunction (cf. 2.42).

\[
\begin{aligned}
&\int d^3 r_1 d^3 r_2 \ldots d^3 r_n \psi_V^*(\{r_i, \sigma_i\}) \hat{V} \psi_V(\{r_i, \sigma_i\}) \\
&= \int d^3 r_1 d^3 r_2 \ldots d^3 r_n \psi_V^*(\{r_i, \sigma_i\}) V(r_1) \psi_V(\{r_i, \sigma_i\}) \\
&= \int d^3 r_1 d^3 r_2 \ldots d^3 r_n \psi_V^*(\{r_i, \sigma_i\}) \psi_V(\{r_i, \sigma_i\}) V(r_1) \\
&\quad \quad = \int d^3 r_1 \rho(r_1) V(r_1) \\
&\quad \quad = \int d^3 r \rho(r) V(r). \quad (2.50)
\end{aligned}
\]
Thus (2.49) becomes

\[
\int d^3r \rho(r)V(r) - \int d^3r \rho(r)V'(r) < \int d^3r \rho'(r)V'(r) - \int d^3r \rho'(r)V(r)
\]

\[
= \int d^3r \rho(r)[V(r) - V'(r)] < \int d^3r \rho'(r)[V'(r) - V(r)]
\]

\[
= \int d^3r [\rho(r) - \rho'(r)][V(r) - V'(r)] < 0. \tag{2.51}
\]

We have started from the assumption that the two potentials \( V(r) \) and \( V'(r) \) are different. However, if the two densities are the same everywhere, that would break the inequality. Therefore, no two linearly independent potential functions produce the same ground state density. The requirement of linear independence excludes the cases where two potentials are related by only a constant offset or scale factor. Both potentials would produce the same density function in these cases.

### 2.4.3 Definition of the density functional

Define the functional

\[
F[\rho(r)] = \min_{\psi(\{r_i\},\{\sigma_i\}) \rightarrow \rho(r)} \langle \psi(\{r_i\},\{\sigma_i\}) | \hat{T} + \hat{W} | \psi(\{r_i\},\{\sigma_i\}) \rangle
\]

\[
\equiv \int d^3r V(r)\rho(r) + F[\rho(r)] \geq E[\rho_{GS}]. \tag{2.54}
\]

i.e. the minimum value of the expectation over all possible \( \psi(\{r_i\},\{\sigma_i\}) \) which yield the density \( \rho(r) \). Define \( E_{GS}, \psi_{GS}(\{r_i\},\{\sigma_i\}) \) and \( \rho_{GS}(r) \) as the ground state energy, wavefunction and density of \( \hat{H}_V \), related by the Schrödinger equation

\[
\hat{H}_V | \psi_{GS}(\{r_i\},\{\sigma_i\}) \rangle = E_{GS} | \psi_{GS}(\{r_i\},\{\sigma_i\}) \rangle. \tag{2.53}
\]
If \( \rho(r) = \rho_{GS}(r) \), the equation becomes

\[
E[\rho_{GS}(r)] = \int d^3r V(r)\rho_{GS}(r) + F[\rho_{GS}(r)]
\]

\[
= \langle \psi_{GS}(\{r_i\}, \{\sigma_i\})|\hat{T} + \hat{W} + \hat{V}|\psi_{GS}(\{r_i\}, \{\sigma_i\}) \rangle
\]

\[
= E_{GS}.
\]

If \( \rho_{GS}(r) \) can be calculated or approximated, that is enough information to calculate \( E_{GS} \) without the wavefunction.

### 2.4.4 The Kohn-Sham Scheme

The Hohenberg-Kohn theorem provides a formalism for determining the ground state energy of a system based only on the density function \( \rho(r) \), but provides no insight into how \( \rho(r) \) might be determined. In practice, the density function is found iteratively, from some initial guess.

Furthermore, the Hohenberg-Kohn energy functional derived from the many-body Schrödinger equation defined in the previous section remains computationally intractable for all but the simplest systems. The first step in the Kohn-Sham scheme is to repartition the energy functional into terms which are more easily calculated.

\[
E[\rho(r)] = T_0[\rho(r)] + \int d^3r \rho(r)[V_{ext}(r) + \frac{1}{2}\Phi(r)] + E_{XC}[\rho(r)]
\]

where \( T_0[\rho(r)] \) is the kinetic energy that a system with density \( \rho(r) \) would have if there were no electron-electron interactions, \( V_{ext}(r) \) is the external potential due to nucleus-electron Coulomb interactions, \( \Phi(r) \) is the classical Coulomb potential for two electrons. \( E_{XC}[\rho(r)] \) is the ‘exchange-correlation’ functional.

Although \( T_0[\rho(r)] \) is not the true kinetic energy of the interacting many-body system, there are two advantages to using it. First, the difference between \( T_0[\rho(r)] \) and the true kinetic energy is often relatively small. The main advantage to using \( T_0[\rho(r)] \) is that this quantity can be solved exactly, relegating any corrections necessary to retrieve the true kinetic energy to \( E_{XC}[\rho(r)] \).
In fact, $E_{XC}[\rho(r)]$ is the only term in the above energy functional which is not known exactly for arbitrary $\rho(r)$. Many approximate exchange-correlation functionals have been proposed, some of which will be explored in later sections.

Taking the functional derivative of equation 2.58 produces

$$
\frac{\delta E[\rho(r)]}{\delta \rho(r)} = \frac{\delta T_0[\rho(R)]}{\delta \rho(r)} + V_{ext}(r) + \Phi(r) + \frac{\delta E_{XC}[\rho(r)]}{\delta \rho(r)} = \mu \tag{2.59}
$$

where $\mu$ is the Lagrange multiplier associated with conservation of particle number. Compare this to the corresponding equation for a non-interacting system in some other system-dependent potential

$$
\frac{\delta E[\rho(r)]}{\delta \rho(r)} = \frac{\delta T_0[\rho(R)]}{\delta \rho(r)} + V(r) = \mu \tag{2.60}
$$

the two equations are equivalent if

$$
V(r) = V_{ext}(r) + \Phi(r) + \frac{\delta E_{XC}[\rho(r)]}{\delta \rho(r)}. \tag{2.61}
$$

Thus, the problem has been converted from a system of many interacting particles to a system of non-interacting particles in an effective potential $V(r)$. The solution for $V(r)$ can be found by solving the Kohn-Sham equations

$$
\left[-\frac{1}{2}\nabla^2 + V(r)\right] \psi_i(r) = \epsilon_i \psi_i(r). \tag{2.62}
$$

The Kohn-Sham equations have the same mathematical form as the single particle Schrödinger equation. But $V(r)$ is not required to correspond to any real system.

The solution method follows an iterative form:

1. Construct some initial guess for $\rho(r)$.
2. Use this $\rho(r)$ to find the effective potential $V(r)$ via (2.61).
3. Use this $V(r)$ to solve the Kohn-Sham equations (2.62).
4. Find a new density from $\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$.
5. Go back to step 2 with the new density, until the density converges to within some tolerance of the minimum of the parameter space.
2.4.5 The Local Density Approximation

The simplest approximation for the exchange-correlation functional is the local density approximation (LDA), i.e. an energy functional which depends only on the electron density $\rho(r)$.

$$E_{XC}^{LDA}[\rho(r)] = \int d^3r \rho(r) \epsilon_{XC}[\rho(r)]$$  \hspace{1cm} (2.63)

where $\epsilon_{XC}[\rho(r)]$ is the exchange-correlation energy per particle of a homogeneous electron gas of density $\rho(r)$. This idea goes all the way back to Dirac’s time[38], but it was not until sufficient computational power existed to find numerical solutions to the Kohn-Sham equations that particular LDA exchange-correlation functionals like that of Perdew and Zunger,[39] emerged.

2.4.6 The Local Spin Density Approximation

The LDA was quite successful as an approximation technique, and improved the results of DFT calculations that used it. However, it was quickly refined to include spin degrees of freedom

$$E_{XC}^{LSDA}[\rho_{\uparrow}(r), \rho_{\downarrow}(r)] = \int d^3r \rho(r) \epsilon_{XC}[\rho_{\uparrow}(r), \rho_{\downarrow}(r)]$$  \hspace{1cm} (2.64)

where $\rho_{\uparrow}(r)$ and $\rho_{\downarrow}(r)$ represent the density of electrons with spin up and spin down, respectively. The is known as the local spin density approximation (LSDA), and many LDA techniques have been subsequently adapted to include spin effects, e.g. that of Perdew and Wang[40] This separation of the electron density by spin allows for explicit dependence of $\epsilon_{XC}$ on electron spin effects. Most notably, an LSDA allows the exchange-correlation functional to treat exchange more robustly, since exchange only occurs between particles in the same spin state.

2.4.7 The Generalised Gradient Approximation

Another approximation to the exchange-correlation functional is the generalised gradient approximation (GGA).[41, 42] The difference between GGA and LDA is the introduction of
2.4 Density functional theory

The inclusion of the density gradient in the calculation of the exchange-correlation functional produces a far more accurate approximation to $E_{XC}$ than the same calculation using LDA or LSDA. The results can even be qualitatively different. Of course, the difference GGA makes to the calculation is dependent on the amount of variation in the ground state density function, i.e. the closer the real system is to a homogeneous electron gas, the less benefit is obtained from a GGA over an LDA. Especially, GGA provides a better ground state energy for spatially localised states such as molecular orbitals. The difference between GGA and LDA is smaller but can still be significant in systems with delocalised states such as an infinite crystal of a simple metal.

2.4.8 Basis functions

There are a number of basis sets used in DFT calculations. The two most common, simplest examples are plane waves of the form

$$ f(k) = Ae^{ik \cdot r} \quad (2.66) $$

and spatially localised functions centred on nuclear positions or bonding regions between nuclei. One particular computational implementation of DFT used in this work, SIESTA, uses numerical atomic orbitals of this form.[43] Molecular orbitals are then constructed from linear combinations of these atomic orbitals (the LCAO method). The specific functions that comprise each atomic orbital are of the form

$$ f(r)Y_{nl}(\theta, \phi) \quad (2.67) $$

where $f(r)$ is some function of radius only, and $Y_{nl}(\theta, \phi)$ are the spherical harmonics. The
radial function is typically of the form

\[ f(r) = \sum_i A_i e^{(-\zeta i r^n)} \]  

(2.68)

where \( A \) is chosen to normalise the electron density, \( n \) is either 1 (Slater type) or 2 (Gaussian type), and \( \zeta \) is a parameter that uniquely defines each basis function. An atomic orbital defined by only one such function (i.e. only one term in the sum) is said to be single-\( \zeta \), or SZ. In practice, double-\( \zeta \) (DZ) or even triple-\( \zeta \) (TZ) basis sets are used. These basis functions are often combined with a small component from an atomic orbital of the next higher angular momentum, to describe spin polarisation of an atomic orbital. Such basis sets are described as \( N - \zeta \) plus polarisation, or NZP. DZP is a very commonly-used basis set, providing a balance between spanning a large enough subspace of the problem to find accurate solutions and minimising the computational effort required to arrive at these solutions. Basis functions where \( n = 1 \) are known as Slater-type functions, whereas basis functions where \( n = 2 \) are Gaussian-type functions. Plane wave based basis sets are also common.

### 2.4.9 Pseudopotentials

Atoms with electrons occupying orbitals across more than one principal quantum number (i.e. everything except H and He) can have the electronic wavefunction separated into core and valence electrons. Core electrons do not contribute significantly to interatomic behaviour, and thus it would be desirable from a computational efficiency perspective not to treat them explicitly. The contribution of core electrons to the electron-electron interaction potential of the valence electrons can be approximated by the introduction of pseudopotentials,[44] defined to asymptotically approach the true interaction potential of the core electrons at a certain, specified convergence radius \( r_c \). The accuracy of this method is usually comparable to the accuracy inherent to the LDA and GGA.[45–47]
2.4.10 Computational implementations

Over the course of the research reported in this thesis, I used three different software implementations of DFT solving code, NRLMOL, SIESTA and Quantum-espresso.

NRLMOL\cite{48–53} was developed by Mark Pederson in circa 1990, at a time when few DFT codes were freely available. Like all the codes described in this work, NRLMOL has its strengths and weaknesses. NRLMOL is the only code of the three that allows all-electron calculations (i.e. without the use of pseudopotentials), making it an excellent choice for determining the accuracy of pseudopotentials for particular chemical systems. NRLMOL is also the only code that can exploit the geometric symmetry of the system studied, greatly reducing the computational cost of a calculation wherever it may be used. Unfortunately, ET molecules in the crystalline environment do not possess such a symmetry. NRLMOL automatically selects basis sets for its calculations, which approximate the accuracy (and number of degrees of freedom) of quadruple-$\zeta$ plus polarisation (QZP) basis sets. NRLMOL’s greatest weakness is the inability to model full crystals using a unit cell and periodic boundary conditions, and therefore cannot calculate band structures.

SIESTA\cite{54} was developed by a team at Universidad Autónoma de Madrid to be an efficient, easy to use code for calculating molecular and crystal properties. Its primary strength is the ability to efficiently calculate properties for large chemical systems, even up to thousands of atoms. It achieves this by using localised basis functions that explicitly fall off to zero beyond a particular cutoff radius, as opposed to basis functions based on exponential falloff at large distances. SIESTA uses a numerical atomic orbital basis set. SIESTA is also capable of calculating band structures by defining a unit cell and applying periodic boundary conditions.

Quantum-espresso\cite{55} (or just Espresso) is a relatively new DFT solving code that possesses most of the features of SIESTA, including the ability to perform band structure calculations. It is also open source, making it accessible to anyone (NRLMOL requires registration and SIESTA is distributed freely to academic users). Espresso differs from the other two codes in that it implements a plane-wave basis set, i.e. basis functions are defined in k-space instead of real space. The computational tradeoff with plane wave basis sets is the relative
simplicity and speed of the calculations involved versus the large number of basis functions required to achieve the same accuracy as with localised basis functions. The accuracy of the basis set is defined by the user by specifying an energy cutoff, indicating the highest energy plane wave to be included in the calculation.

2.4.11 Benchmark calculations

As an initial test of the software code and for pedagogical reasons, I performed a number of calculations on simpler systems to see what level of accuracy I could expect from DFT for various properties. For these tests, I used three sets of chemical compound, the first-row dimers (H$_2$, Li$_2$, Be$_2$, B$_2$, C$_2$, N$_2$, O$_2$, and F$_2$), simple organic molecules (ethane, ethene and ethyne) and simple metals (Ni, Cu, Pd, Au). The calculated properties I used to measure the accuracy of the code were the equilibrium bond lengths, the binding energy for the first-row dimers, the ionisation potential for the simple organics, and the valence band widths and overall band structure for the metals.

The first-row dimers are in fact very sensitive to the tunable parameters in a DFT code, e.g. the basis set, pseudopotentials, exchange-correlation functional, and density function approximation. For this reason, the first-row dimers proved to be a poor test of the effectiveness of DFT for the chemical systems studied in this thesis. I established that GGA calculations were marginally more accurate than LSDA calculations and that a DZP basis set was sufficient. However the fine tuning of the basis set and pseudopotential parameters required to return accurate values of the bond length or binding energy revealed a truism of many multivariable optimisation problems – optimising a system for one variable or situation tends to de-optimise it for others. A calculation that gives a very good bond length likely gives a poor binding energy, and vice versa. Similarly, a parameter set optimised for a first-row homonuclear dimer is unlikely to be accurate in any other chemical environment.

The simple organic molecules were a very different story. Bond lengths, bond angles and ionisation potentials of ethane, ethene and ethyne were calculated to remarkable agreement with experiment using default parameters automatically generated by the code. This was
Figure 2.10: VASP (left) and Quantum-espresso (right) are both plane-wave based DFT codes. The two are compared here with a band structure of simple crystalline copper, calculated in a GGA. The two results agree qualitatively and quantitatively, despite differences that emerge due to discretisation, the type of exchange-correlation functional, and the construction of the pseudopotentials. The discrepancy in the position of the Fermi energy between the graphs is most likely due to different input conditions regarding how the density of states is calculated. In both cases, the Fermi energy $E_F$ is found by satisfying $\int_{-\infty}^{E_F} D(E) dE = N$, where $D(E)$ is the density of states per unit energy and $N$ is the number of valence electrons per unit cell.

very encouraging, given that ET molecules are also organic and therefore likely to be well-suited to the same parameters.

The benchmark calculations on first-row dimers and simple organics were performed in NRLMOL and SIESTA. The benchmarks on the simple metals were performed in Espresso. The resulting band structures and features such as the valence band width were in excellent agreement with previous calculations available in the literature, and with similar benchmark calculations performed by Elvis Shoko (See Figure (2.10)).[56]

Having verified the effectiveness of DFT for calculating energetic properties of various chemical systems, I proceeded to apply these techniques to the analysis of these properties in the ET and Pd(dmit)$_2$ salts.
Parametrisation of the one site Hubbard model
for an ET monomer

The background information presented in the previous chapter is applied from here on, where finally the process of finding particular parameter values for the Hubbard model parameters for particular materials is described and the results presented.

3.1 The Hubbard model and density functional theory

Two different classes of ET salt need to be distinguished. In the first class, which includes the \( \kappa, \beta, \) and \( \beta' \) phases, the ET molecules are strongly dimerised. The intra-dimer dynamics are typically integrated out of the effective low-energy Hamiltonian, to leave one with a half-filled Hubbard model, where each dimer is treated as a site.\(^7\) However, if one is to satisfactorily parameterise this effective Hamiltonian, one must first understand the intra-dimer dynamics. In the second class of ET salt, which includes the \( \alpha, \beta'', \) and \( \theta \) phases, the dimerisation is weak or absent and one is forced to consider a quarter-filled Hubbard model in which each site corresponds to a single monomer.\(^5\)

It is convenient, for our purposes, to write the (extended) Hubbard model in the form

\[
\hat{H} = \sum_i \hat{H}_i + \sum_{ij} \hat{H}_{ij},
\] 

(3.1)
3.1 The Hubbard model and density functional theory

where $\hat{H}_i$ are the terms that depend on the physics of a single ET molecule and $\hat{H}_{ij}$ are the terms coupling more than one ET molecule. Let us assume that

$$\hat{H}_i = E_0 + \epsilon_m \hat{c}_{i\sigma}^{\dagger} \hat{c}_{i\sigma} + U_m \hat{c}_{i\uparrow}^{\dagger} \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^{\dagger} \hat{c}_{i\downarrow},$$

where $\hat{c}_{i\sigma}^{\dagger}$ annihilates (creates) a particle with spin $\sigma$ on site $i$, $E_0$ may be thought of as the energy due to the ‘core electrons’ and the nuclei, $\epsilon_m$ is the site energy for site $i$, and $U_m$ is the effective Coulomb repulsion between electrons on site $i$, whose interpretation I shall discuss presently. (In general $E_0$, $\epsilon_m$, and $U_m$ may be different of different sites, but site labels have been supressed in order to simplify notation. The subscript $m$ serves to remind us that we are dealing with the Hubbard parameters for a monomer rather than dimeric parameters.) Note that I do not consider vibronic interactions; however these can be included straightforwardly via the Hubbard-Holstein model. Calculations of the vibronic interactions have been reported by several groups.[58–64] Also note that, I will not discuss the form or the parameterisation of $\hat{H}_{ij}$ below. Most previous studies of $\hat{H}_{ij}$ have been based on the extended Hückel or tight binding approximation, which neglect all two-body terms in $\hat{H}_{ij}$.[65–68]

It is convenient to separate $U_m$ into two terms

$$U_m = U_m^{(v)} - \delta U_m^{(p)},$$

where $U_m^{(v)}$ is the value of $U_m$ for an isolated ET molecule in vacuum and $\delta U_m^{(p)}$ is the reduction of $U_m$ when the molecule is placed in the polarisable crystalline environment. $\delta U_m^{(p)}$ has been successfully calculated for alkali doped fullerenes,[69–71] oligo-acene and thiopenes,[72] and TTF-TCNQ.[73] Perhaps the simplest system for which to calculate $\delta U_m^{(p)}$ is the alkali doped fullerides. This system has (approximate) spherical symmetry and a large intermolecular spacing relative to the size of the molecule. $\delta U_m^{(p)}$ has been calculated for the alkali doped fullerides both by assuming that the crystal is a dielectric medium and by assuming that each molecule in the crystal contributes to $\delta U_m^{(p)}$ only via the classical polarisability tensor appropriate to that molecule.[69–71, 74] These calculations show that
\( \delta U_m^{(p)} \) can be a significant fraction of \( U_m^{(v)} \), perhaps as much as a half.[69–71, 74] However, the calculation of the polarisation correction to the \( U \) for the ET salts is a much more difficult problem. First, the systems have very low symmetry. Second, many ET salts have polymeric counterions, therefore it is not possible to approximate the anion layers by a lattice of dipoles. Third, ET molecules are separated by distances typical of \( \pi \)-stacking in aromatic compounds (\( \sim 3.5-4 \) Å), i.e., distances that are quite small compared to the size of the molecule. This invalidates the approximations based on well-separated dipoles or an effective mean-field dielectric medium that have been successfully applied to the fullerenes. Therefore, I limit my attention to the calculation of \( U_m^{(v)} \). Clearly the calculation of \( \delta U_m^{(p)} \) is an important problem that must be solved before a full parameterisation of the Hubbard model for ET salts can be completed. Interestingly, Cano-Cortés et al.[73] have recently reported a calculation of \( \delta U_m^{(p)} \) for TTF-TCNQ, which manifests some of these problems, where the dipole moment is associated with individual atoms rather than entire molecules.

It is often stated that the Hubbard \( U \) is the Coulomb repulsion between two electrons in the highest occupied molecular orbital (HOMO) of an ET molecule. This is, indeed, often a conceptually helpful way to think about the Hubbard \( U \). However, if one were to take this literally it would be natural to equate \( U_m^{(v)} \) with the zeroth Slater-Condon parameter, i.e., the Coulomb integral,

\[
F_0 = \int d^3r_1 \int d^3r_2 \frac{\rho_\uparrow(r_1)\rho_\downarrow(r_2)}{|r_1 - r_2|},
\]

(3.4)

where \( \rho_\sigma(r) \) the density of spin \( \sigma \) electrons at the position \( r \) in the HOMO of the ET molecule. \( F_0 \) is rather different from the Hubbard \( U \). To see this, recall that the Hubbard model is an effective low-energy Hamiltonian and therefore the Hubbard parameters are renormalised. Assuming that \( U_m^{(v)} = F_0 \) is equivalent to simply ignoring the high energy degrees of freedom not contained in the Hubbard model. This is clearly inadequate: \( F_0 \) is the unrenormalised value of \( U_m^{(v)} \). In principle one should derive the effective low-energy Hamiltonian by explicitly integrating out the high energy degrees of freedom. However, this is not practicable in this context for all but the simplest systems.[74–81] Therefore, one should construct the effective low-energy Hamiltonian so as to capture the relevant degrees of freedom and parameterise this effective Hamiltonian appropriately. I shall now review
3.1 The Hubbard model and density functional theory

how to do this for the Hubbard model.

In the ET salts the HOMO of the ET molecule is, on average, three quarters filled with electrons or, equivalently, one quarter filled with holes. Therefore, the hole parameters are of more physical relevance than the electron parameters, as I shall discuss further below.

One might also consider the Taylor series for the dependence of the energy on the ‘classical’ (i.e., not quantised) charge in terms of electrons,

\[
E(q) \simeq E(0) + \left. \frac{\partial E}{\partial q} \right|_{q=2^-} (2 - q) + \frac{1}{2} \left. \frac{\partial^2 E}{\partial q^2} \right|_{q=2^-} (2 - q)^2, \tag{3.5a}
\]

or holes,

\[
E(q) \simeq E(2) + \left. \frac{\partial E}{\partial q} \right|_{q=0^+} q + \frac{1}{2} \left. \frac{\partial^2 E}{\partial q^2} \right|_{q=0^+} q^2, \tag{3.5b}
\]

where \( q = 2^- \) indicates the limit as \( q \to 2 \) from below and \( q = 0^+ \) indicates the limit as \( q \to 0 \) from above. Again, \( E(q) \) can be calculated from DFT by calculating the total energy of the relevant charge states. It then follows from (2.23) that the classical \( U \) is given by

\[
U_{mc} = \left. \frac{\partial^2 E}{\partial q^2} \right|_{q=2^-}. \tag{3.6}
\]

Similarly, the classical site energies are

\[
\epsilon_{mc} = \left. \frac{\partial E}{\partial q} \right|_{q=2^-} \quad \text{and} \quad \xi_{mc} = \left. \frac{\partial E}{\partial q} \right|_{q=0^+}, \tag{3.7}
\]

as one expects from Janak’s theorem[82]. We, therefore, are left with the classical results in terms of electrons,

\[
E(q) \simeq E(0) + \epsilon_{mc}(2 - q) + \frac{1}{2} U_{mc}(2 - q)^2. \tag{3.8a}
\]

and holes,

\[
E(q) \simeq E(2) + \xi_{mc}q + \frac{1}{2} U_{mc}q^2. \tag{3.8b}
\]

Note, however, that \( \xi_{mc} = - (\epsilon_{mc} + 2U_{mc}) \) in contrast to Eq. (2.26). This is a manifestation of the failure of classical approximation for the site energy.

The density functional formalism can be applied to fractional numbers of electrons.[82, 83]
Therefore one can calculate the energy for a large number of charge states and find the best fit values of $E(0)$, $\epsilon_{mc}$, $\xi_{mc}$, and $U_{mc}$ in Eqs. (3.8), which is operationally more satisfactory than determining the two free parameters ($\xi_m$ and $U_m$ determine $\epsilon_m$) from two data points [$E(1) - E(0)$ and $E(2) - E(0)$]. Of course this method suffers from the fact that, unlike Eqs. (2.23), (2.24), and (2.26), Eqs. (3.8) are not exact.

Eqs. (3.8) give remarkably good fits to the fractional charge data (c.f. Fig. 3.1). Furthermore, $U_{mc}^{(v)}$ is an extremely accurate approximation to $U_m^{(v)}$ (typically the two values differ by $\lesssim 1\%$). In contrast $\epsilon_{mc}$ and $\xi_{mc}$ are not good approximations to $\epsilon_m$ and $\xi_m$. This is a consequence of my use of an approximate generalised gradient approximation (GGA)[41, 42] exchange-correlation functional. It is known that for the exact functional the energies of states with fractional charges are linear interpolations between integer charge states[82–85]. In contrast for local functionals, such as the local density approximation (LDA) or that of Perdew, Burke and Erzenhof (PBE)[89], $E(q)$ is a convex function[83, 86–88]. This is closely related to the self-interaction error and leads to the delocalisation error in local functionals and the band gap problem[83–88]. Indeed, for the exact functional $\epsilon_m = \epsilon_{mc}$, $\xi_m = \xi_{mc}$, and $U_{mc}^{(v)} = 0[82–88]$.

### 3.2 Computational methods

The process of calculating the Hubbard model parameters is highly non-trivial, and several steps are necessary to prepare the appropriate input to the DFT code.

#### 3.2.1 Preparing the input

The most significant component of the input to a DFT code is the position of the nuclei in the system. All of the ET crystals discussed in this thesis had their structures determined by X-ray crystallography and the results published in the literature[21, 90–105].

The crystallographic data provides nuclear positions for all atoms except hydrogen. Hydrogen atoms were introduced to the system by an initial guess, then relaxation by molecular dynamics during the DFT process. The initial guess was based on the assumptions that a
3.2 Computational methods

C-H bond is approximately 1.1 Å long, and that the two C-H bonds, along with the existing C-C and C-S bonds, form an approximate tetrahedron. The nuclear positions were reported as fractions of the co-ordinate system of the crystal axes, a, b, and c. From knowledge of the angles between the crystal axes, α, β, and γ, and the magnitude of the crystal axes, a, b, and c, I deduced the co-ordinate transform from fractional crystal co-ordinates to Cartesian. The convention I used was: a is parallel to the x-axis and b lies on the x–y plane, leaving only c with a z component.

This stage was necessary because while it is possible to specify input to DFT code in fractional crystal co-ordinates, this is only useful if you intend to simulate the full unit cell of the crystal. For a cluster, such as the single ET molecules examined here, it is necessary to deliberately select only those atoms from the crystallography data that correspond to one of the ET molecules, and to place that molecule in a unit cell so large it is effectively isolated from neighbouring cells.

The nuclear positions for the ET monomers studied appear in the supplementary information of [1].

3.2.2 Computing the model parameters

I used DFT to calculate the total energies and HOMO charge densities of ET molecules in various conformations and charge states. In order to compare the effects of different basis sets and pseudopotentials (including no pseudopotential) I made use of two different implementations of DFT, SIESTA[54] and NRLMOL.[46, 48–53] In each case a separate self-consistent field (SCF) calculation was performed at every charge state studied.

SIESTA calculations were performed using the PBE exchange-correlation functional.[89] A triple-ζ plus single polarisation (TZP) basis set of Sankey numerical atomic orbitals[106] was used for all atoms. These orbitals are confined to some radius r_c from their centres, which introduces a small increase to the energy of each orbital. The value of r_c was determined by specifying the maximum allowed increase in energy due to this cutoff, which I limited to 2 mRy. The convergence of the integration mesh is determined by specifying an effective plane-wave energy cutoff for the mesh, which I set to 250 Ry. The initial spin moments
on each atom were arranged antiferromagnetically, i.e., with opposite signs on neighbouring atoms, wherever possible. All SIESTA calculations reported below used pseudopotentials constructed according to the improved Troullier-Martins (TM2) method.\cite{107,108}

NRLMOL performs massively parallel electronic structure calculations using Gaussian orbital methods. I again used the PBE exchange correlation functional. For these calculations I shall use Porezag-Pederson (PP) basis sets,\cite{46} which have been carefully optimized for the PBE-GGA energy functional using variational energy criteria. As discussed in Ref. \cite{46}, for each atom, the basis sets are optimized with respect to the total number of Gaussian decay parameters, and with respect to variation of these parameters and the contraction coefficients. These are roughly of triple to quadruple zeta quality.\cite{46} As compared to other Gaussian basis sets, a key improvement in the PP optimization scheme is that the resulting basis sets satisfy what is now referred to as the $Z_{10}^{10/3}$ theorem. This theorem \cite{46} discusses proper scaling of the Gaussian exponents near the nuclei as a function of atomic charge. It has been shown that the resulting PP basis sets exhibit no superposition error and alleviate the need for counterpoise corrections in weakly bound systems. I report both all-electron calculations and calculations using pseudopotentials for C and S atoms performed in NRLMOL. These pseudopotentials were constructed using the method of Bachelet, Hamann and Schlüter (BHS).\cite{109}

In section 3.3 I shall discuss various schemes for relaxing these atomic positions and for calculating $U_m(v)$, therefore I delay defining these methods to that section. The total energy was then computed for charge states ranging from charge neutral (doubly-occupied HOMO), to the 2+ charge state (the same orbital unoccupied) in increments of 0.1 electrons. The resulting 21 data points per molecule were then fitted to a quadratic function by the method of least squares, from which values of $U_m(v)$, $\epsilon_m$ and $\xi_m$ were extracted according to Eqs. (3.8). $U_m$, $\epsilon_m$ and $\xi_m$ were calculated from integer charge states according to Eqs. (2.23), (2.24), and (2.26).

Calculations of the Coulomb integral, $F_0$, make use of the orbitals from the corresponding calculations. The integrals in Eq. (3.4) were calculated in the charge neutral state on a $55 \times 30 \times 20$ mesh using the trapezoidal rule. I have also investigated finer meshes and the calculations were found to be well converged with respect to the number of integration
3.3 Geometry optimisation, pseudopotentials, basis sets, and calculation methods

Results of calculations of $U^{(v)}_m$ and $F_0$ performed using TZP basis sets and TM2 pseudopotentials appear in Table 3.1. For these calculations I took the nuclear positions of the C and S atoms from x-ray scattering experiments[21] on $\beta$-ET$_2$I$_3$ and the nuclear positions of the H atoms were relaxed using the conjugate-gradient method. Henceforth, I shall refer to this method of determining the nuclear geometry as ‘experimental’. Both eclipsed and staggered conformations (c.f. Fig. 3.2) are observed experimentally[21] and I present results for both conformations. However, there is no significant differences between the eclipsed and staggered conformations in either $U^{(v)}_m$ or $F_0$. There does not appear to be significant difference in the calculated values of $U^{(v)}_m$ and $U^{(v)}_{mc}$. Similar results are found for the other geometries studied.

Several groups[110–115] have reported calculated values of $F_0$ or $U^{(v)}_m$ previously. I summarise their results in Table 3.2. It can be seen from Tables 3.1 and 3.2 that there is broad agreement between the values calculated by a range of different levels of theory, basis sets, and starting from different experimental geometries. Across all of the calculations $F_0$ is $\sim 40\%$ larger than $U^{(v)}_m$. This over-estimation has been attributed to the fact that $F_0$ neglects orbital relaxation,[111–115] i.e., the tendency of the orbital to change as its population changes. Conceptually, this is very important. It stresses that the sites in the Hubbard model do not correspond to any particular ‘orbital’ of the ET molecule, as these orbitals change in response to charge fluctuations, etc. in the crystal. $F_0$ is, in fact, simply the first order
Table 3.1: Comparison of different methods of calculating the effective monomer on-site Coulomb repulsion for ET. No significant differences are found between $U^{(v)}_{mc}$ and $U^{(v)}_m$ from the DFT calculations. This result has been confirmed for all of the geometries studied below. Further, no significant differences are found between the two conformations. $F_0$ is significantly larger than $U^{(v)}_m$, in qualitative agreement with previous results from wavefunction based methods (c.f. Table 3.2). The nuclear geometry is that seen 'experimentally' in $\beta$-(ET)$_2$I$_3$ for both the eclipsed and staggered conformations. The calculations use TZP basis sets and TM2 pseudopotentials. All values are in eV.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Eclipsed</th>
<th>Staggered</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U^{(v)}_{mc}$</td>
<td>4.12</td>
<td>4.07</td>
</tr>
<tr>
<td>$U^{(v)}_m$</td>
<td>4.17</td>
<td>4.08</td>
</tr>
<tr>
<td>$F_0$</td>
<td>5.40</td>
<td>5.35</td>
</tr>
</tbody>
</table>

approximation to $U^{(v)}_m$.[116, 117] Therefore the true value of $U^{(v)}_m$ contains many non-trivial quantum many-body effects which are absent in $F_0$ beyond just orbital relaxation.[116] As I am presenting DFT calculations it is also interesting to consider the self interaction correction (SIC), which is absent in wavefunction methods. If the SIC per electron were constant then the SIC would cancel entirely when $U^{(v)}_m$ is calculated from Eq. (2.23). Of course this is only approximately true, but nevertheless suggest that the SIC is less important for $U^{(v)}_m$ than for $F_0$.

Now let us consider the effect of different calculation schemes on the Hubbard parameters. To that end, results are presented for values of $U^{(v)}_m$ for ET molecules in geometries taken from $\beta$-(ET)$_2$I$_3$, calculated with two major modifications to the input. The first modification is to relax the nuclear coordinates. I have investigated three methods of determining the nuclear coordinates. The first nuclear co-ordinate set is the ‘experimental’ geometry defined above, i.e., the experimental positions are used for the C and S atoms, but the H atoms, which are not seen in x-ray scattering experiments, are relaxed. The second set was obtained by relaxing all the nuclear positions in the charge neutral state and holding that geometry fixed for all later SCF calculations at different charge states. This set is labelled ‘frozen’. The third set of nuclear co-ordinates was obtained by relaxing all nuclear positions in each charge state. This set is labelled ‘relaxed’. The second modification to the computational method is to perform the calculations with different basis sets and pseudopotentials.

Results for the experimental, frozen, and relaxed geometries appear in Table 3.4 using a
Table 3.2: Previously reported calculations of the Coulomb energy ($F_0$) and $U_m^{(v)}$ of ET. These calculations were performed at various levels of theory, using various basis sets and with geometries taken from x-ray crystallography experiments on various different materials. $F_0$ is significantly larger than $U_m^{(v)}$, consistent with my results. I make use of the following abbreviations in the above table: HF (Hartree-Fock); RHF (restricted Hartree-Fock); and VB (valence bond). Fortunelli and Painelli[111–113] calculated $F_0$ for ET dimers in different charge states, $q$. All energies are in eV.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set</th>
<th>Atomic geometry from</th>
<th>$F_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF[110]</td>
<td>SBK-31G*</td>
<td>$\kappa-(ET)_2Cu[N(CN)]_2Cl$[118]</td>
<td>5.90</td>
</tr>
<tr>
<td>HF[110]</td>
<td>SBK-31G*</td>
<td>$\kappa-(ET)_2Cu[N(CN)]_2Br$[119]</td>
<td>5.90</td>
</tr>
<tr>
<td>HF[110]</td>
<td>SBK-31G*</td>
<td>$\kappa-(ET)_2Cu[N(CN)]_2I$[118]</td>
<td>5.83</td>
</tr>
<tr>
<td>RHF ($q = 4$)[111–113]</td>
<td>6-31G**</td>
<td>$\kappa-(ET)_2Cu[N(CN)]_2Br$[119]</td>
<td>5.44</td>
</tr>
<tr>
<td>RHF ($q = 2$)[111–113]</td>
<td>6-31G**</td>
<td>$\kappa-(ET)_2Cu[N(CN)]_2Br$[119]</td>
<td>6.40</td>
</tr>
<tr>
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<td>$\kappa-(ET)_2Cu[N(CN)]_2Br$[119]</td>
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<tr>
<td>Mean $F_0$</td>
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<td>5.84</td>
</tr>
<tr>
<td>Std. dev.</td>
<td></td>
<td></td>
<td>0.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set</th>
<th>Atomic geometry from</th>
<th>$U_m^{(v)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF[111–113]</td>
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</tr>
<tr>
<td>VB-HF[114]</td>
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</tr>
<tr>
<td>VB-HF[114]</td>
<td>AM1</td>
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<td>3.83</td>
</tr>
<tr>
<td>VB-RHF[115]</td>
<td>AM1</td>
<td>$\beta-(ET)_2I_3[120]$</td>
<td>3.90</td>
</tr>
<tr>
<td>VB-RHF[115]</td>
<td>DZ &amp; 4-31G</td>
<td>$\beta-(ET)_2I_3[120]$</td>
<td>4.61</td>
</tr>
<tr>
<td>Mean $U_m^{(v)}$</td>
<td></td>
<td></td>
<td>4.15</td>
</tr>
<tr>
<td>Std. dev.</td>
<td></td>
<td></td>
<td>0.37</td>
</tr>
</tbody>
</table>

variety of basis sets and pseudopotentials. The TZP basis sets consistently gives $U_m^{(v)} \sim 0.2$ eV smaller than the PP basis sets; similar small differences are seen in $\epsilon_m$ and $\xi_m$. However, the trends between the different geometries are reproducible between the two calculations. These differences may be related to the fact that the PP orbitals are optimised for each charge state whereas the TZP numerical orbitals are the same for every charge state. This additional degree of freedom reduces the curvature of $E(q)$ which reduces $U_m^{(v)}$ and hence $U_m^{(v)}$. Whether pseudopotentials are used or all electron calculations are performed does not have a significant effect on the results. The experimentally measured[121] gas phase ionisation energy of ET is 6.2 eV, in reasonable agreement with my calculated value of $\xi_m$. Note, however, that $\xi_{mc}$ is significantly smaller than the experimental value.

The trend between the different geometries is more interesting. Each time a geometry
Table 3.3: Pseudopotential parameters for the TM2 pseudopotentials used in SIESTA calculations were generated with the ATOM utility. These are the input parameters, taken from the header of the .psf files that were created. All pseudopotentials were generated by ATOM version 3.2.2, set for use with the PBE exchange-correlation functional, with no relativistic correction. The carbon pseudopotential uses ‘pcec’ pseudocore-correction. Hydrogen and sulphur do not use core corrections. Spin polarisation was not used. The electron population, $n$, and convergence radii, $r$, for each angular momentum state follow.

<table>
<thead>
<tr>
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<th>Orbital</th>
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<th>$r$</th>
</tr>
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<td>3p</td>
<td>2.00</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
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<td>0.99</td>
</tr>
<tr>
<td></td>
<td>4f</td>
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<td>0.99</td>
</tr>
</tbody>
</table>

Relaxation is performed $U_m^{(v)}$ is reduced. This results from the increased number of degrees of freedom when more geometry relaxation is allowed. This can be seen from the plot of the energy for different charge states in Fig. 3.1. For both of these curves both the geometry relaxation and SCF calculation were performed using the TZP basis sets and TM2 pseudopotentials. The two $q = 0$ results are therefore, in fact, the same data point. As the charge is varied away from $q = 0$ the geometry remains fixed in ‘frozen’ calculation but relaxes in the ‘relaxed’ calculation, thus the energy of ‘relaxed’ data is lower than that of the ‘frozen’ calculation $q > 0$. This effect gets larger as $q$ increases, thus $U_m^{(v)}$ is smaller in the ‘relaxed’ data than for the ‘frozen’ calculation. The physical content of this result is simply the fact that intramolecular vibronic couplings act to lower $U_m^{(v)}$. [58] However, one should expect this effect to be rather stronger in vacuo than in the crystalline environment where the motion of the molecule is significantly constrained.

Thus we must face the question: should one use the ‘experimental’, ‘frozen’, or ‘relaxed’ geometry to calculate $U_m^{(v)}$? I argue that the ‘experimental’ geometry gives the most useful information. Firstly, there are small differences in the reported geometries for different
ET salts, and one would like to understand the effect of these on a single molecule before considering the effects of changes in the crystal structure on the emergent physics of the crystal. Secondly, the experiments effectively ‘integrate over’ all of the relevant charge states and therefore provide an ‘average’ conformation. Thirdly, the experiments naturally include the effects on the molecular conformation due to the crystalline environment, which are absent from in vacuo calculations. Therefore I shall now move on to consider the value of $U_m^{(v)}$ found for the ‘experimental’ geometry found in x-ray scattering experiments from a wide range of different ET salts.

### 3.4 Impurity scattering, polymorphism and chemical pressure

Let us begin by studying polymorphism in (ET)$_2$I$_3$, for which the experimental literature contains more reported polymorphs than any other salt of ET. Table 3.5 summarises the calculated values of the Hubbard parameters and the Coulomb integral for ET molecules in ‘experimental’ geometries[21, 90–93] taken from the $\alpha$, $\beta$, $\kappa$, and $\theta$ polymorphs of (ET)$_2$I$_3$. All of the calculations in this section were performed using TZP basis sets and TM2 pseudopotentials. There is little variation in $U_m^{(v)}$ across any of the polymorphs ($U_m^{(v)} = 4.22 \pm 0.09$ eV). For the $\alpha$, $\kappa$, and $\theta$ polymorphs $\xi_m$ is extremely uniform ($\xi_m = 4.840 \pm 0.008$ eV) but $\xi_m$ is somewhat larger in the $\beta$ polymorph. More interestingly $\xi_m$ is 0.12 eV larger for the staggered conformation of $\beta$-(ET)$_2$I$_3$ than it is for eclipsed conformation (the two conformations are sketched in Fig. 3.2). To understand the significance of this result we must first briefly review a few experiments on $\beta$-ET$_2$I$_3$ and a little of the theory of impurity scattering in unconventional superconductors.

The application of hydrostatic pressure, $P$, to $\beta$-ET$_2$I$_3$ has a dramatic effect on the superconducting critical temperature, $T_c$. At ambient pressure $T_c \sim 1.5$ K but when the applied pressure reaches $P \sim 1$ kbar a discontinuous increase in $T_c$ ($\sim 7$ K) is observed. The low $T_c$ state ($P \lesssim 1$ kbar) is labelled the $\beta_L$ phase and the high $T_c$ state ($P \gtrsim 1$ kbar) is labelled the $\beta_H$ phase. When the pressure on the $\beta_H$ phase is decreased the material does
not return to the $\beta_L$ phase but rather $T_c$ is seen to further increase. Below $T \sim 130$ K the resistivity of the $\beta_H$ phase is found to undergo a discontinuous decrease while no such anomaly is found in the $\beta_L$ phase.[123] Incommensurate lattice fluctuations have been observed in the $\beta_L$ phase but they are absent in the $\beta_H$ phase below $T \sim 130$ K.[124] The incommensurate lattice fluctuations are stabilised by variations in the conformational ordering of the terminal ethylene groups of the ET molecules and thus can only exist in the presence of disorder.[125] For a more detailed review of this phenomenology see Ref. [65].

It is well known that non-magnetic disorder can lead to the suppression of $T_c$ in unconventional (‘non-s-wave’) superconductors, as the ET salts are believed to be.[7, 126] The details of this suppression are described by the Abrikosov-Gorkov equation,[127]

$$\ln \left( \frac{T_{c0}}{T_c} \right) = \psi \left( \frac{1}{2} + \frac{\hbar}{4\pi k_B T_c \tau} \right) - \psi \left( \frac{1}{2} \right), \quad (3.9)$$

where $T_{c0}$ is the superconducting transition temperature of a pure sample, $1/\tau$ is the quasiparticle scattering rate and $\psi$ is the digamma function. Considering only the contributions to $\tau$ from terminal ethylene group disorder then

$$\frac{\hbar}{\tau} = N_s \pi D(E_F) |\Delta \xi_m|^2, \quad (3.10)$$

where, $N_s$ is the number of molecules in the staggered conformation, $D(E_F)$ is the density of states at the Fermi energy, and $\Delta \xi_m = 0.12$ eV is the difference between the values of $\xi_m$ calculated in the staggered and eclipsed phases. Note that as the ET salts are quarter filled with holes (three quarters filled with electrons) $\xi_m$, not $\epsilon_m$, is the relevant quantity here. It has previously been shown[122] that over both the $\beta_H$ and $\beta_L$ phases of $\beta$-ET$_2$I$_3$ the critical temperature scales with the residual resistivity, which is proportional to the contribution to $1/\tau$ from impurity scattering, as predicted by the Abrikosov-Gorkov equation.

My finding that the staggered and eclipsed conformations have a small but important difference in $\xi_m$ shows that the disorder in the conformational degrees of freedom of the terminal ethylene groups of the ET molecules, required to stabilise the lattice fluctuations, is responsible for the suppression of $T_c$ in the $\beta_L$ phase. The terminal ethylene disorder
increases the quasiparticle scattering rate and that this leads to the observed different $T_c$'s of the $\beta_H$ and $\beta_L$ phases. A simple calculation based on the derivation in Ref. [122] shows that the calculated value of $\Delta \xi_m$ accounts for the observed differences between the critical temperatures and residual resistivities of the $\beta_H$ and $\beta_L$ phases with a few percent of the molecules staggered conformation.

It is interesting that such significant differences are caused by the conformation changes in ET. Fig. 3.3 shows isosurfaces containing $\sim 90\%$ of the charge density of the Kohn-Sham orbitals corresponding to the HOMOs of eclipsed and staggered ET molecules at the ‘experimental’ geometries found in $\beta$-ET$_2$I$_3$. Note that there is very little electron density on the terminal ethylene groups, which are the only parts of the molecule in different positions in the ‘experimental’ eclipsed and staggered phases. Furthermore, there are no significant changes between the HOMO electron densities on the other atoms between the two conformations.

It is well known that changing the anion in ET salts (which changes the unit cell volume) has a remarkably similar effect to applying a hydrostatic pressure. Therefore, changing the anion is often referred to as ‘chemical pressure’. [7, 65] Both hydrostatic and chemical pressure have dramatic effects on the phase diagram of ET salts. This is typically understood in terms of a variation of Hubbard model parameters, e.g., the ratio $U/t$, where $t$ is the relevant hopping integral. [7, 57] Therefore, I shall now consider the changes in the Hubbard parameters caused by changing the anion. Figs. 3.4, 3.5, and 3.6 show the calculated values of, respectively, $U_m^{(v)}$, $\epsilon_m$, and $\xi_m$ for ‘experimental’ geometries taken from x-ray scattering experiments on crystals with a wide range of anions and several different polymorphs. The crystallographic data sets[21, 90–105] used to determine the nuclear positions include data taken at a range of temperatures and under different pressures.

It can be seen from Fig. 3.4 that the none of the changes to the crystal (anion, polymorphism, conformation, temperature, or hydrostatic pressure) have a significant effect on $U_m^{(v)}$, indeed over all of the structures studied here $U_m^{(v)} = 4.2 \pm 0.1$ eV (here, and below, the reported ‘error’ is simply one standard deviation in the data and does not reflect systematic errors, particularly those arising from my approximate density functional calculation of the total molecular energies).

An important question is: how large does variation of $U/t$ have to be in order to explain
the experimental results? It is possible to estimate this from strongly correlated theories of the Hubbard model. Both the resonating valence bond theory,[129–131] and cluster extensions to dynamical mean-field theory[132, 133] suggest that $U/t$ is required to vary by perhaps a factor of two in order to explain the experimental phase diagram, although variational quantum Monte Carlo results suggest that the variation need not be quite this large.[134]

The results show that $U^{(v)}_m$ is a transferable property and does not play any significant role in the ‘chemical pressure’ effects observed in the behaviour of the ET salts. This means that either the chemical pressure comes from $\delta U^{(p)}_m$ and/or the elements of $H_{ij}$, or else the simple Hubbard model description is not sufficient to describe the behaviour of the ET salts.

Figs. 3.5 and 3.6 show that the variation of $\epsilon_m = -9.2 \pm 0.1$ eV and $\xi_m = 5.0 \pm 0.2$ eV is not much larger than that in $U^{(v)}_m$. However, it is known that the ET salts are very sensitive to disorder[135, 136] therefore these subtle effects may lead to much more profound effects in the extended system than the variation in $U^{(v)}_m$. Note also that while the Hubbard $U$ is the same for electrons and holes the site energies are rather different, as expected from the discussion in section 3.1, when $U$ is large.

The similarity between the electronic states of ET molecules in the conformations found in different salts is further emphasised by fact that the Kohn-Sham orbital corresponding to the HOMO is essentially the same in all of the molecules studied. As an example of this I plot the electronic density of the HOMO for an ET molecule in the ‘experimental’ geometry taken from a crystal of $\kappa$-ET$_2$Cu[N(CN)$_2$]Cl in Fig. 3.3. This can be seen to be remarkably similar to the equivalent plots for $\beta$-ET$_2$I$_3$ (also shown in Fig. 3.3) despite the fact the polymorph and the anion are different.

The data for these Hubbard model parameter figures is provided in table form below. The different ET crystals are more easily compared when presented this way, especially the difference between $F_0$ and $U^{(v)}_m$. 
3.4 Impurity scattering, polymorphism and chemical pressure

Figure 3.1: Dependence of the energy of an ET molecule on the charge of the molecule. Two different geometries are studied. The ‘frozen’ geometry is relaxed from that found experimentally[21] in \( \beta-(ET)_2I_3 \) in the neutral charge state and then held fixed during the self-consistent field (SCF) calculations at different charge states. For the ‘relaxed’ data the nuclear geometry is relaxed separately for each charge state. The energies are exactly equal by definition in the charge neutral state; for other charge states the nuclear relaxation lowers energies. This reduces the curvature of \( E(q) \), i.e., lowers \( U_{mc}^{(v)} \) and hence \( U_{m}^{(v)} \). It can be seen that for both the ‘frozen’ and the ‘relaxed’ geometries the energy of the fractional charge states is extremely well described by the classical quadratic functions, Eqs. (3.8). In contrast it is known that for the exact functional the energy of molecules with fractional charges is a linear interpolation between the integer charge states.[82–85] To an excellent approximation \( U_{mc}^{(v)} = U_{m}^{(v)} \) whereas \( \epsilon_{mc} \) and \( \xi_{mc} \) are not good approximations to \( \epsilon_{m} \) and \( \xi_{m} \). In contrast for the exact functional \( \epsilon_{m} = \epsilon_{mc} \), \( \xi_{m} = \xi_{mc} \), and \( U_{mc}^{(v)} = 0 \). This incorrect result is a manifestation of the delocalisation error of DFT and closely related to the band gap problem.[83–88] These calculations use TZP basis sets and TM2 pseudopotentials.
Figure 3.2: The eclipsed and staggered conformations of the ET molecule. The major difference is the relative orientation of the terminal ethylene groups.
Table 3.4: Calculated bare and renormalised parameters for the Hubbard model for ET monomers under various geometry relaxation schemes and with different pseudopotentials, basis sets and codes (see section 3.2). The 'experimental' geometry is that reported for an ET molecule in $\beta$-(ET)$_2$I$_3$[21] measured at 298 K, with the H atom (not observed in x-ray crystallography) positions relaxed. The 'frozen' coordinate system was relaxed in the charge neutral state and held fixed for other charge states. The relaxed geometry was optimised at every charge state. All geometry relaxations were carried out in calculations using TZP basis functions and TM2 pseudopotentials; I have also carried out the relaxations in using the other methods in the table and find no significant differences. The abbreviation pseudo. (for pseudopotential) is used in this table and others below. The RMSE is taken from the fit to the classical Eqs (3.8). All values are in eV.

<table>
<thead>
<tr>
<th>Structure</th>
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<th>Basis</th>
<th>Pseudo.</th>
<th>$U_m^{(v)}$</th>
<th>$\epsilon_m$</th>
<th>$\xi_m$</th>
<th>$U_{mc}^{(v)}$</th>
<th>$\epsilon_{mc}$</th>
<th>$\xi_{mc}$</th>
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</tr>
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<td>TM2</td>
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<td>TM2</td>
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Table 3.5: Calculated bare and renormalised parameters for the Hubbard model for an ET molecule at the 'experimental' geometry observed at ambient temperature and pressure in various polymorphs of (ET)$_2$I$_3$. The changes in conformation due to the crystal packing structure do not have a large effect on the value of $U^{(v)}_m$. The calculated $\xi_m$ is larger for the $\beta$ polymorph than the others explored, indeed $\xi_m$ varies by less than 1% among the other polymorphs. Note that there is a significant difference between the values of $\xi_m$ in the eclipsed and staggered conformations in the $\beta$ phase. This is consistent with the effects of conformational disorder on $\beta$-ET$_2$I$_3$.[122] The calculations use TZP basis sets and TM2 pseudopotentials. All values are in eV.

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<th>Crystal type</th>
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<th>$F_0$</th>
<th>$U^{(v)}_m$</th>
<th>$\epsilon_m$</th>
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Table 3.6: Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different 'experimental' geometries observed in crystals of $\alpha$-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, $X$ taken at a range of temperatures, $T$. The structural data obtained by Bender et al.[90] and Emge et al.[91] contains three distinct monomer structures, one staggered and two eclipsed. The eclipsed conformations are numbered arbitrarily in order to distinguish them. The calculations use TZP basis sets and TM2 pseudopotentials.

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<th>T (K)</th>
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Figure 3.3: Orthographic projections of the isosurface of the HOMO of the ET molecule in ‘experimental’ geometries taken from (a) eclipsed $\beta$-(ET)$_2$I$_3$, (b) staggered $\beta$-(ET)$_2$I$_3$, and (c) $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl. Note the great similarity of the HOMOs corresponding to the ‘experimental’ geometries from eclipsed and staggered $\beta$-(ET)$_2$I$_3$ and the small electronic density on the terminal ethylene group, which is involved in the change between the eclipsed and staggered conformations. Further, the HOMOs of the ET molecule in the ‘experimental’ geometries taken from $\beta$-ET$_2$I$_3$ and $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl are remarkably similar despite the fact that this geometry is taken from a different crystal polymorph with a different anion. This is consistent with my finding that the changes in the conformation of the ET molecule, in different polymorphs and in crystals with different anions, do not significantly affect $U_m^{(v)}$. Colour indicates the sign of the Kohn-Sham orbital. All isosurfaces are $\pm 0.07 \text{Å}^{-3/2}$ and calculated in the charge-neutral state. These calculations use TZP basis sets and TM2 pseudopotentials. Animations showing different isosurfaces are available online.\cite{128}
Figure 3.4: The effective Coulomb repulsion between electrons/holes, $U_m^{(v)}$, on an ET monomer in the ‘experimental’ geometries corresponding to different anions, conformations (eclipsed offset to the left, staggered to the right), temperatures, pressures, and crystal polymorphs. Note the limited range (3.9 – 4.4 eV) of the ordinate. $U_m^{(v)}$ does not change significantly across the different (ET)$_2$X crystals and has a mean value of 4.2 ± 0.1 eV. The calculations use TZP basis sets and TM2 pseudopotentials.

Table 3.7: Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of β-(ET)$_2$X. The structural data contains different conformations and come from materials with a range of anions, X. The calculations use TZP basis sets and TM2 pseudopotentials.

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<th>$\epsilon_m$</th>
<th>$\xi_m$</th>
<th>$U_m^{(v)}$</th>
<th>$\epsilon_{mc}$</th>
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3.4 Impurity scattering, polymorphism and chemical pressure

Figure 3.5: The site energy for electrons, $\epsilon_m$, on an ET monomer in the 'experimental' geometries corresponding to different anions, conformations (eclipsed offset to the left, staggered to the right), temperatures, pressures, and crystal polymorphs. Note the range of the ordinate. The mean value is $\epsilon_m = -9.2 \pm 0.1$ eV. The calculations use TZP basis sets and TM2 pseudopotentials.

Table 3.8: Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different 'experimental' geometries observed in crystals of $\beta''$-$(ET)_2X$. The structural data contains different conformations and come from materials with a range of anions, $X$ and was taken at various temperatures, $T$ (temperatures in K). The calculations use TZP basis sets and TM2 pseudopotentials.

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<th>$\epsilon_m$</th>
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Figure 3.6: The site energy for holes, \( \xi_m \), on an ET monomer in the 'experimental' geometries corresponding to different anions, conformations (eclipsed offset to the left, staggered to the right), temperatures, pressures, and crystal polymorphs. \( \xi_m \) shows only slightly more variation than \( U_m^{(r)} \). However, small changes in \( \xi_m \) are known to have significant effects on the superconducting state observed in ET salts.[135, 136] (Because these ET molecules are quarter filled with holes in the salt, \( \xi_m \), rather than \( \epsilon_m \), is the relevant site energy to consider when discussing the role of disorder.) The mean value is \( \xi_m = 5.0 \pm 0.2 \) eV. The calculations use TZP basis sets and TM2 pseudopotentials.
## 3.4 Impurity Scattering, Polymorphism and Chemical Pressure

Table 3.9: Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of \( \kappa-(ET)_2X \). The structural data contains different conformations and come from materials with a range of anions, \( X \) and was taken at various pressures, \( P \), and temperatures, \( T \) (temperature in K). The calculations use TZP basis sets and TM2 pseudopotentials.

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<td>Std. dev.</td>
<td></td>
<td></td>
<td>0.13</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
<td>0.04</td>
<td>0.06</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Table 3.10: Variation of the bare and renormalised parameters for the Hubbard model for an ET monomer over the different ‘experimental’ geometries observed in crystals of $\theta$-(ET)$_2$X monomers. Two distinct monomers were observed experimentally,[93] they are labelled arbitrarily above but appearing in the crystal in alternating positions. The calculations use TZP basis sets and TM2 pseudopotentials.

<table>
<thead>
<tr>
<th>Anion</th>
<th>$T$ (K)</th>
<th>Conf.</th>
<th>$F_0$</th>
<th>$U_m^{(v)}$</th>
<th>$\epsilon_m$</th>
<th>$\xi_m$</th>
<th>$U_{mc}^{(v)}$</th>
<th>$\epsilon_{mc}$</th>
<th>$\xi_{mc}$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_3$[93]</td>
<td>283-303</td>
<td>eclipsed 1</td>
<td>5.40</td>
<td>4.21</td>
<td>-9.05</td>
<td>4.84</td>
<td>4.15</td>
<td>-11.14</td>
<td>2.84</td>
<td>0.022</td>
</tr>
<tr>
<td>I$_3$[93]</td>
<td>283-303</td>
<td>eclipsed 2</td>
<td>5.36</td>
<td>4.32</td>
<td>-9.24</td>
<td>4.91</td>
<td>4.23</td>
<td>-11.38</td>
<td>2.92</td>
<td>0.032</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>5.38</td>
<td>4.27</td>
<td>-9.15</td>
<td>4.88</td>
<td>4.19</td>
<td>-11.26</td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>Std. dev.</td>
<td></td>
<td></td>
<td>0.03</td>
<td>0.08</td>
<td>0.13</td>
<td>0.05</td>
<td>0.06</td>
<td>0.17</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>
Parametrisation of the two site Hubbard model for an ET dimer

The procedure for calculating parameters for the two site Hubbard model is quite similar to that for the one site model described above. The nuclear positions were transformed from fractional crystal co-ordinates to Cartesian, using the same method as for the one site preparation. However, before the co-ordinate transform, the nuclear positions of a second ET molecule, specifically the nearest neighbour that forms the dimer pair, were found from the symmetry of the crystal. All ET dimer molecules are related to each other by an inversion symmetry and appropriate unit cell translations.

4.1 Computational methods

I used DFT to calculate the total energies of ET dimers in various conformations and charge states. I used the SIESTA[54] implementation of DFT, with the PBE exchange-correlation functional,[89] a triple-ζ plus single polarisation (TZP) basis set (except where I specify otherwise) and basis functions consisting of Sankey type numerical atomic orbitals.[106] The orbital functions were confined to a radius $r_c$ from their centres, which slightly increases the energy of the orbital. The specified maximum allowed increase in energy due to this cutoff was 2 mRy. The convergence of the integration mesh was determined by specifying an effective plane-wave cutoff energy of 250 Ry. The initial spin moments on each atom
were arranged antiferromagnetically wherever possible. I used pseudopotentials constructed according to the improved Troullier-Martins (TM2) method.[107]

Nuclear positions for C and S atoms were obtained from x-ray crystallography.[21, 92, 94, 95, 100, 101, 103, 137] H atoms, which are not observed in x-ray scattering experiments, were relaxed by the conjugate-gradient method. Total DFT energy differences between the relevant charge states \([E(1) - E(0)]\) and \([E(2) - E(0)]\) were equated with the corresponding analytical expressions in Eq. (4.4) to determine the Hubbard parameters. I focus on these ‘experimental’ geometries rather than performing a full relaxation for a number of reasons. Firstly, there are small differences in the reported geometries for different ET salts, and one would like to understand the effect of these. Secondly, the experiments effectively ‘integrate over’ all of the relevant charge states and therefore provide an ‘average’ conformation. Thirdly, the experiments naturally include the effects on the molecular conformation due to the crystalline environment, which are absent from in vacuo calculations.

4.2 The two site extended Hubbard model

Below I present results of DFT calculations for \(U_d^{(v)}\) of dimers in the conformations found in a wide range of \(\kappa\) and \(\beta\) phase ET salts. Similar results hold for \(U_m\), the effective Coulomb repulsion between two holes on the same monomer and \(V_m\) the effective Coulomb interaction between two holes on neighbouring monomers. Below I will primarily discuss the vacuum contributions to these terms, \(U_m^{(v)}\) and \(V_m^{(v)}\).

The effective vacuum intradimer Coulomb energy, \(U_d^{(v)}\), is given by (see, e.g., Ref. [1])

\[
U_d^{(v)} = E(0) + E(2) - 2E(1),
\]  

(4.1)

where \(E(q)\) is the ground state energy of the dimer in vacuum containing \(q\) holes, i.e., with charge \(+q\). Similarly, the effective site energy for holes is given by

\[
\xi_d = E(0) - E(1).
\]  

(4.2)
Below I calculate $E(q)$ via density functional methods.

It is also interesting to consider intradimer dynamics, which can be described via a two site extended Hubbard model,[7]

$$\hat{H} = \sum_{i\sigma} \xi_{mi} \hat{n}_{i\sigma} - t \sum_{\sigma} \left( \hat{h}^\dagger_{1\sigma} \hat{h}_{2\sigma} + h.c. \right) + \sum_{i} U_{mi} \hat{n}_{ii\sigma} + V_{m} \hat{n}_{1\sigma} \hat{n}_{2\sigma}$$

(4.3)

where $\hat{h}^{(i)}_{i\sigma}$ annihilates (creates) a hole on site (monomer) $i$ in spin state $\sigma$, $\xi_{mi}$ is the site energy for holes on site $i$, $\hat{n}_{i\sigma}$ is the number operator for spin $\sigma$ holes on site $i$, $\hat{n}_{ii\sigma} = \sum_{\sigma} \hat{n}_{i\sigma}$, $t$ is the inter-monomer hopping integral, $U_{mi}$ is the effective on-site (monomer) Coulomb repulsion, and $V_{m}$ is the intersite Coulomb repulsion.

The lowest energy eigenvalues of Hamiltonian (4.3) for each charge state are

$$E(0) = 0, \quad (4.4a)$$

$$E(1) = \xi_{m} - \frac{1}{2} \sqrt{4t^{2} + (\Delta \xi_{m})^{2}}, \quad (4.4b)$$

and

$$E(2) = 2\xi_{m} + \frac{1}{3} (2U_{m} + V_{m} - 2A \cos \theta) \quad (4.4c)$$

where $\xi_{m} = \frac{1}{2}(\xi_{m1} + \xi_{m2})$, $A = 12t^{2} + (\Delta U_{m})^{2} + (U_{m1} - V_{m})(U_{m2} - V_{m}) + 3(\Delta \xi_{m})^{2}$, $\cos 3\theta = (U_{m} - 2V_{m})[18t^{2} - (2U_{m1} - U_{m2} - V_{m})(U_{m1} - 2U_{m2} + V_{m}) - 9(\Delta \xi_{m})^{2}] / 2A^{3}$. $\Delta \xi_{m} = \xi_{m1} - \xi_{m2}$, $\overline{U}_{m} = \frac{1}{2}(U_{m1} + U_{m2})$, and $\Delta U_{m} = U_{m1} - U_{m2}$.

I have previously calculated $\xi_{m}$ and $U_{m}^{(c)}$ from the one site Hubbard model for an ET monomer for the experimental observed conformations in all the materials discussed below,[1] therefore one may solve Eqs. (4.4) for $t$ and $V_{m}$ taking $\xi_{m}$ and $U_{m}^{(c)}$ from the monomer calculations. The case of two monomers with different site energies and on-site Coulomb repulsion may be solved by a general method for diagonalising cubic matrix eigensystems.[25] In cases where the two monomers within a dimer have the same geometry (e.g., by symmetry),
Figure 4.1: The HOMO of (ET)$_{2}^{2+}$ (top) and charge neutral (ET)$_{2}$ (bottom), with nuclear positions from the crystal $\beta$-(ET)$_{2}$I$_{3}$. The HOMO of (ET)$_{2}^{2+}$ is the dimer bonding orbital and the HOMO of (ET)$_{2}$ is the antibonding orbital of the two ET HOMOs (cf. Fig. 4.3). The essential difference between the two lies in the relative phase of the orbital function on each molecule. The bonding orbital connects the ET molecules at the S···S contacts (cf. Fig. 3.2). In the antibonding orbital, there are nodes between the S···S contacts.
Figure 4.2: The HOMO of (ET)$_{2}^{2+}$ (top) and charge neutral (ET)$_{2}$ (bottom), with nuclear positions from the crystal \(\kappa\)-(ET)$_{2}$Cu$_{2}$CN$_{3}\). The similarity of the nuclear structures and orbitals between this conformation and the \(\beta\) conformation in Fig. 4.1 highlight the dimer as a common structural unit within two different packing motifs.
Parametrisation of the two site Hubbard model for an ET dimer

Figure 4.3: The HOMO of a charge neutral ET monomer, with nuclear positions from the crystal β-(ET)$_2$I$_3$. This is the orbital from each molecule that contributes to the HOMO of the (ET)$_2$ and (ET)$_2^{2+}$ dimers.

$\xi_{m1} = \xi_{m2} = \xi_m$ and $U_{m1} = U_{m2} = U_m$ and the eigenvalues simplify to

\begin{align}
E(1) &= \xi_m - t \\
E(2) &= 2\xi_m + \frac{1}{2} \left( U_m + V_m - \sqrt{16t^2 + (U_m - V_m)^2} \right),
\end{align}

in which case the solution is straightforward.

In the limit $U_m = V_m = 0$ the two site Hubbard model has two solutions: the bonding state $|\phi_{b\sigma}\rangle = |\phi_{1\sigma}\rangle + |\phi_{2\sigma}\rangle$ and the antibonding state $|\phi_{a\sigma}\rangle = |\phi_{1\sigma}\rangle - |\phi_{2\sigma}\rangle$, where $|\phi_{i\sigma}\rangle = \hat{h}_{i\sigma}|0\rangle$ is a single electron state centred on the $i^{th}$ monomer and $|0\rangle$ is the (particle) vacuum state.

In Figs. 4.1 and 4.2 I plot the HOMOs of ET dimer for the conformations found in β-(ET)$_2$I$_3$ and κ-(ET)$_2$Cu$_2$(CN)$_3$ respectively, in both the charge neutral and the 2+ states. It can be seen that these dimer orbitals are the antibonding and bonding hybrids of the ET monomer HOMO (shown in Fig. 4.3), respectively. The most important difference between the orbital geometries lies in the S···S inter-monomer contacts, which contain nodes in the antibonding orbital, but are connected in the bonding orbital. Thus the DFT picture of the (ET)$_2$ system is remarkably similar to the molecular orbital description of a diatomic molecule,[138] but with the ‘covalent bond’ between the two monomers rather than between two atoms.
4.3 Calculation of the Hubbard model parameters

4.3.1 Basis set convergence

I tested the basis set convergence of the DFT calculations using the conformation observed in $\kappa$-(ET)$_2$Cu(NCS)$_2$ as the test case, with single-ζ (SZ), single-ζ plus polarisation (SZP), double-ζ (DZ), double-ζ plus polarisation (DZP) and TZP basis sets. I also calculated the monomer parameters, $U_m$ and $\xi_m$, in each basis, using the method I previously applied to the ET monomers.[1] The Hubbard model parameters in each basis set are reported in Fig. 4.4. The values of all parameters are well-converged in the TZP basis, except...
\( t \). \( t \) is an order of magnitude smaller than the other parameters, and on the order of both the variation of the other parameters among the basis sets tested and the uncertainty associated with the calculation method. This suggests that extracting \( t \) from band structure calculations\cite{139, 140} is probably a more reliable method of estimating the hopping integrals in these systems.

4.3.2 Variation of the intra-dimer hopping integral

The above considerations notwithstanding, I report my intra-dimer hopping integrals in values in Fig. 4.5 for the purpose of comparison to previous estimates from DFT and Hückel methods (see Table 4.1). For \( \beta \)-(ET)\(_2\)X crystals, \( t = 0.54 \pm 0.15 \) eV. For \( \kappa \)-(ET)\(_2\)X crystals, \( t = 0.59 \pm 0.10 \) eV. These values are at the high end of the range presented in Table 4.1, but are, nevertheless, consistent with previous estimates.

4.3.3 Variation of the intra-dimer Coulomb repulsion

Consider the variation of the effective Coulomb interactions across the conformations found in different materials, beginning with \( U_d^{(v)} \). In Fig. 4.6 I show the values of \( U_d^{(v)} \) for the conformations observed experimentally in a variety of ET crystals. Of particular note are the three data points corresponding to different possible conformations of \( \beta \)-(ET)\(_2\)I\(_3\). In the ET molecule the terminal ethylene groups may take two relative orientations known as the staggered and eclipsed conformations (cf. Fig. 3.2). \( U_d^{(v)} \) is smallest when both ET molecules are in the staggered conformation. Conversely, the largest \( U_d^{(v)} \) for this crystal occurs when both ET molecules are eclipsed, with intermediate \( U_d^{(v)} \) values for the case with one staggered and one eclipsed ET molecule. This trend is repeated in the \( \kappa \)-phase crystals, where two data sets (corresponding to different temperatures at which the nuclear positions were determined) for \( \kappa \)-(ET)\(_2\)Cu[CN]\(_2\)I provide data for both conformations.

The mean value of \( U_d^{(v)} \) for the \( \beta \) phase crystals is \( 3.19 \pm 0.07 \) eV, and the mean \( U_d^{(v)} \) for the \( \kappa \) phase crystals is \( 3.23 \pm 0.09 \) eV. The quoted error is one standard deviation over the full set of conformations studied. The difference between the two values of \( U_d^{(v)} \) is \( \sim 1\% \), and well within the error ranges. This suggests that \( U_d^{(v)} \) takes the same value, 3.2 eV, in all
4.3 Calculation of the Hubbard model parameters

In phase ET salts. This result is significantly larger than the value of $U_d^{(v)}$ obtained from Hückel calculations ($\sim 0.5–2$ eV), as I shall discuss below.

4.3.4 Variations in site energy and the role of disorder

A number of experiments have shown that disorder has strong effects on both the normal state and superconducting properties of organic charge transfer salts. [135, 136, 141–146] There has been relatively little work on the effect of the random $U$ Hubbard model. Conclusions drawn from studies in one dimension[147, 148] cannot be straightforwardly generalised to higher dimensions. Mutou[149] used dynamical mean field theory to study the metallic phase of the random $U$ Hubbard model. However, he did not consider the effect of a random $U$ on either superconductivity or the Mott transition, which are the primary concerns in the organic charge transfer salts. However, Mutou concluded that for small impurity concentrations, Kondo-like effects mean that the random $U$ Hubbard model is significantly different from the virtual crystal approximation to the random $U$ Hubbard model, which describes the system in terms of an average $U$. The only study[150] I am aware of that discusses superconductivity in the random $U$ Hubbard model treats the negative $U$ model, which is not realistic for the organic charge transfer salts. Litak and Győrffy[150] studied a model where some sites have $U = 0$ and others have a negative $U$. They find that superconductivity is suppressed above at certain critical concentration of $U = 0$ sites. Therefore, it is not clear what implications my finding of small changes in $U_d^{(v)}$ and hence $U_d$ has for the physics of the organic charge transfer salts. However, it is interesting to ask what role this plays in the observed role of disorder in suppressing superconductivity[135] and driving the system towards the Mott transition.[142] In this context it would be interesting know whether the changes in the optical conductivity found by Sasaki et al. in samples with disorder induced by x-ray irradiation[151] can be explain in terms of a randomly varying $U_d$.

To understand the role of conformational disorder in terms of an effective Hamiltonian built up from ET dimers one must also understand the effect of conformational disorder on the effective dimer site energy (for holes), $\xi_d$. This is straightforwardly found from the DFT calculations described above via Eq. (4.2) and the results are reported in Fig. 4.7. In the
Born approximation the scattering rate for a random pattern of non-magnetic impurities, represented by the potential \( V(r) = \sum_i u_i \delta(\mathbf{R}_i - r) \), where \( \mathbf{R}_i \) is the location of the \( i^{\text{th}} \) impurity, is \( \hbar/\tau = \sum_i N_i \pi D(E_F) |u_i|^2 \) (Ref. [152]). Eq. (4.6) follows immediately as, for conformational impurities, \( u_i = \Delta_i \xi_d \). The effective scattering rate due to conformational disorder is given by

\[
\frac{\hbar}{\tau} = \sum_i N_i \pi D(E_F) |\Delta_i \xi_d|^2,
\]  

(4.6)

where \( i \) labels the type of impurity (both staggered or mixed; the ground state conformation is both eclipsed), \( N_i \) is number of impurities of type \( i \), \( D(E_F) \) is the density of states at the Fermi level, and \( \Delta_i \xi_d \) is the difference between \( \xi_d \) for \( i \) type impurities and \( \xi_d \) of eclipsed dimers.

In quasi-2D systems, \( D(E_F) \) is simply related to the cyclotron electron mass[153] by the relation

\[
D(E_F) = \frac{m_e}{2\pi \hbar^2}
\]  

(4.7)

and in the presence of interactions Luttinger’s theorem[154] for a Fermi liquid produces

\[
D(E_F) = \frac{m^*}{2\pi \hbar^2}
\]  

(4.8)

where \( m^* \) is the effective mass. From quantum oscillation measurements, Wosnitza et al.[155] found that \( m^*/m_e = 4.2 \) in \( \beta\)-ET\(_2\)I\(_3\), where \( m_e \) is the electron rest mass. From Shubnikov-de Haas measurements in \( \kappa\)-ET\(_2\)Cu[N(CN)\(_2\)]Br Caulfield et al.[156] found that \( m^*/m_e = 6.4 \). The scattering rate \( \tau \) can be found from measurement of the interlayer residual resistivity, \( \rho_0 \), by the relation[157]

\[
\rho_0 = \frac{\pi \hbar^4}{2e^2 m^* c t_\perp^2 \tau}
\]  

(4.9)

where \( c \) is the interlayer lattice constant taken from the relevant x-ray scattering measurements[21, 137] and \( t_\perp \) is the interlayer hopping integral, which has previously been estimated from experimental data for both \( \kappa\)-ET\(_2\)Cu[N(CN)\(_2\)]Br (Ref. [155]) and \( \beta\)-ET\(_2\)I\(_3\) (Ref. [135]). Using
these parameters I calculated the scattering rate in both the $\beta_L$ and $\beta_H$ phases of $\beta$-ET$_2$I$_3$ from the low temperature values of $\rho_0$ reported by Ginodman et al.[123] The scattering rate due to conformational impurities, $\tau^{-1}_c$ is then $\tau^{-1}_c = \tau^{-1}_H - \tau^{-1}_L$, where $\tau_L$ ($\tau_H$) is the quasiparticle lifetime in the $\beta_L$ ($\beta_H$) phase. Given my calculated values of $\Delta \xi_d$ an $\sim 8\%$ concentration of staggered impurities would be required to cause this scattering rate. From a similar calculation comparing the residual resistivity measured in a single sample of $\kappa$-ET$_2$Cu[N(CN)$_2$]Br cooled at different rates I find that a $\sim 2\%$ concentration of staggered impurities would be sufficient to explain the rise increase in residual resistivity observed in the experiment utilising the fastest cooling over that performed with the slowest cooling rate. X-ray scattering experiments[146] find that $3 \pm 3\%$ of the ET molecules are in the staggered conformation at 9 K, which is entirely consistent with my result. However, Wolter et al.’s[146] argument that this impurity concentration is too small to cause the observed effects of disorder in not sustained by the above calculations. Rather I find that all of the suppression in $T_c$ is entirely consistent with this degree of disorder.

### 4.3.5 Variations in inter-monomer Coulomb repulsion

In Fig. 4.8 I show the distribution of the calculated values of $V_m^{(v)}$. The mean value of $V_m^{(v)}$ for the $\beta$ phase crystals is $2.69 \pm 0.13$ eV, while the mean value for the $\kappa$ phase crystals is $2.72 \pm 0.09$ eV. Again, the difference between the values is small ($\sim 2\%$) compared to the distribution for each polymorph. Therefore, $V_m^{(v)}$ is essentially the same across all of the conformations studied, with a mean value of $2.71 \pm 0.10$ eV.

Previous calculations of $U_d^{(v)}$ based on both Huckel and DFT methods[92, 101, 124, 139, 140, 158–163] have assumed that $U_m^{(v)} \rightarrow \infty$ and $V_m^{(v)} = 0$. Substituting these conditions into Eqs. (4.1) and (4.5) yields $U_d^{(v)} = 2t$. Literature values of $U_d^{(v)}$ based on this approximation are presented in Table 4.1 for comparison with my DFT results. It can be seen that this assumption yields values of $U_d^{(v)}$ that are significantly smaller than those I have calculated above (cf. Fig. 4.6). However, I have previously found[1] that $U_m^{(v)} = 4.2 \pm 0.1$ eV. Comparing this with the above results we see that $U_m^{(v)}/V_m^{(v)} \sim 1.5$, in contradiction of the assumption that $U_m^{(v)} \gg V_m^{(v)}$. Hence $U_m^{(v)} \gg |2t|$. 


Table 4.1: Previous estimates of $U_d^{(v)}$ for various $\beta$- and $\kappa$-phase ET salts. These values were obtained from both Hückel and density functional methods under the assumptions $U_m^{(v)} \rightarrow \infty$ and $V_m^{(v)} = 0$, which yields $U_d^{(v)} = 2t$. These estimates substantially underestimate the actual value of $U_d^{(v)}$ (see Fig. 4.6) as $U_m^{(v)} \sim V_m^{(v)}$. The two site extended Hubbard model produces values of $t$ on the same order of magnitude as these Hückel calculations. One should also note the wide scatter between the different Hückel calculations, even between different studies of the same material.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Method</th>
<th>$U_d^{(v)}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-(ET)$_2$I$_3$</td>
<td>Hückel[158]</td>
<td>0.49</td>
</tr>
<tr>
<td>$\beta$-(ET)$_2$IBr$_2$</td>
<td>Hückel[124]</td>
<td>0.98</td>
</tr>
<tr>
<td>$\beta$-(ET)$_2$ICl$_2$</td>
<td>Hückel[124]</td>
<td>1.04</td>
</tr>
<tr>
<td>$\beta$-(ET)$_2$I$_3$</td>
<td>Hückel[158]</td>
<td>0.49</td>
</tr>
<tr>
<td>$\beta$-(ET)$_2$CH(SO$_2$CF$_3$)$_2$</td>
<td>Hückel[159]</td>
<td>0.88-0.90</td>
</tr>
<tr>
<td>$\beta$-(ET)$_2$[OsNOCl$_5$]</td>
<td>Hückel[160]</td>
<td>2.10</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl</td>
<td>DFT[139]</td>
<td>0.4</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br</td>
<td>Hückel[161]</td>
<td>0.45</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu(NCS)$_2$</td>
<td>Hückel[162]</td>
<td>0.48</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu(NCS)$_2$</td>
<td>Hückel[101]</td>
<td>0.14</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu(NCS)$_2$</td>
<td>Hückel[163]</td>
<td>0.46</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu(NCS)$_2$</td>
<td>DFT[140]</td>
<td>0.83</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu(NCS)$_2$</td>
<td>DFT[139]</td>
<td>0.4</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br</td>
<td>Hückel[163]</td>
<td>0.49</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu$_2$(CN)$_3$</td>
<td>Hückel[163]</td>
<td>0.45</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu$_2$(CN)$_3$</td>
<td>DFT[140]</td>
<td>0.85</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$Cu$_2$(CN)$_3$</td>
<td>DFT[139]</td>
<td>0.4</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$I$_3$</td>
<td>Hückel[163]</td>
<td>0.49</td>
</tr>
<tr>
<td>$\kappa$-(ET)$_2$I$_3$</td>
<td>Hückel[92]</td>
<td>0.22</td>
</tr>
</tbody>
</table>

If we instead make the assumption $U_m^{(v)} \simeq V_m^{(v)} \gg |t|$, then Eqs. (4.1) and (4.5) give

$$U_d^{(v)} \approx \frac{1}{2}(U_m^{(v)} + V_m^{(v)}).$$

(4.10)

Substituting in the mean values of $U_m^{(v)}$ and $V_m^{(v)}$ gives $U_d^{(v)} = 3.41$ eV. This result is close to (within 6% of) my calculated value of $U_d^{(v)}$. Therefore, this is a reasonable approximation for the ET salts. Further, this shows that the result that $U_d^{(v)}$ does not vary significantly because of changes in conformation between different salts or polymorphs is a consequence of the fact that neither $U_m^{(v)}$ or $V_m^{(v)}$ vary significantly because of changes in conformation between different salts or polymorphs.
4.4 General comments on the ET dimer parameterisation

The effective Coulomb repulsion terms in the Hubbard model are essentially the same for all of the ET conformations studied. I found that $U_d^{(v)} = 3.22 \pm 0.09$ eV, $V_m^{(v)} = 2.71 \pm 0.10$ eV. The value of $U_d^{(v)}$ is significantly larger than previous estimates based on the extended Hückel formalism or DFT under the assumptions $U_m^{(v)} \to \infty$ and $V_m^{(v)} = 0$. This can be understood because I have shown that $U_m^{(v)} \sim V_m^{(v)}$ and hence $U_d^{(v)} \approx \frac{1}{2}(U_m^{(v)} + V_m^{(v)})$.

The lack of variation of $U_d^{(v)}$ between the two polymorphs and when the anion is changed is interesting in the context of theories of these organic charge transfer salts based on the Hubbard model. These theories require $U_d/W$ to vary significantly as the anion is changed (chemical pressure) and under hydrostatic pressure. Therefore my results show that either $\delta U_d^{(p)}$ or $W$ must vary significantly under chemical and hydrostatic pressure, or else these theories do not provide a correct description of the $\beta$ and $\kappa$ phase organic charge transfer salts. This is particularly interesting as fast cooling has been shown to drive $\kappa$-ET$_2$Cu[N(CN)$_2$]Br to the insulating side of the metal-insulator transition.[142]

I have also studied the effects of conformational disorder on these parameters, which is found to be quite small, consistent with the often subtle effects of conformational disorder observed in these materials. The largest changes are found in the geometries taken from $\beta$-(ET)$_2$I$_3$, which shows the strongest effects of conformational disorder. It is also interesting to note the presence of a systematic variation in $U_d^{(v)}$ is caused by conformational disorder. As there has been relatively little work on the random $U$ Hubbard model it is difficult to speculate what effects this has on the low temperature physics of the organic charge transfer salts at present.

Given that DFT band structure parametrisations of the interdimer hopping integrals have recently been reported for several organic charge transfer salts,[139, 140] the outstanding challenge for the parametrisation of the Hubbard model in these systems is the accurate calculation of $\delta U_d^{(p)}$. The bandwidth in both the $\beta$ (Ref. [164]) and $\kappa$ (Refs. [139, 140]) phase salts is around 0.4-0.6 eV. Therefore, my finding that $U_d^{(v)}$ is significantly larger than has been realised previously shows that $\delta U_d^{(p)}$ must be significant as if $U_d \simeq U_d^{(v)}$ then
all of these materials would be well into the Mott insulating regime. Thus $\delta U_d^{(p)}$ must significantly reduce $U_d$ in order for the, observed, rich phase diagram to be realised. This is consistent with comparisons of DMFT calculations to optical conductivity measurements on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$, which suggest that $U_d = 0.3$ eV.[165] Further, $\delta U_d^{(p)}$ may be quite sensitive to the crystal lattice and therefore may be important for understanding the strong dependence of these materials on chemical and hydrostatic pressure.
4.4 General comments on the ET dimer parameterisation

Figure 4.5: Inter-monomer hopping term, $t$, for various ET dimers. The mean value for $\beta$-(ET)$_2$X crystals is $t = 0.54 \pm 0.15$ eV, although there is an apparent grouping of $\beta$–(ET)$_2$I$_3$ about $t \sim 0.64$ eV while the other $\beta$– crystals have $t \sim 0.35$ eV. For $\kappa$-(ET)$_2$X crystals, the value of $t = 0.59 \pm 0.10$ eV. These results suggest that in terms of the delocalisation effect of dimerisation, either $\beta$-(ET)$_2$I$_3$ more closely resembles the $\kappa$- ET crystals than its fellow $\beta$- crystals, or $t$ is essentially the same for both crystal polymorphs and the low value of $t$ for $\beta$-(ET)$_2$AuI$_2$ and $\beta$-(ET)$_2$IBr$_2$ is unusual.
Figure 4.6: The effective intra-dimer Coulomb repulsion, $U_d^{(v)}$, for various ET dimers. The $x$-axis separates the data by source crystal polymorph ($\beta$ or $\kappa$), and by the terminal ethylene group conformation of each ET molecule in the dimer. $U_d^{(v)}$ does not change significantly across the different ET crystals examined. For $\beta$-(ET)$_2$X crystals, $U_d^{(v)} = 3.19 \pm 0.07$ eV. For $\kappa$-(ET)$_2$X crystals, $U_d^{(v)} = 3.23 \pm 0.09$ eV. The difference in $U_d^{(v)}$ between the two crystal polymorphs is $\sim 1\%$. Therefore, there is no significant dependence of $U_d^{(v)}$ on the dimer geometry associated with different crystal polymorphs.
4.4 General comments on the ET dimer parameterisation

Figure 4.7: Dimer hole site energy, $\xi_d$, for various ET dimers. For $\beta$-(ET)$_2$X crystals, the mean value is $\xi_d = 4.45 \pm 0.10$ eV. For $\kappa$-(ET)$_2$X crystals, the mean value is $\xi_d = 4.46 \pm 0.14$ eV. The mean value for the whole data set is $\xi_d = 4.46 \pm 0.13$ eV. The effect of conformation on $\xi_d$ is significantly larger for $\beta$-(ET)$_2$I$_3$ ($\sim 10\%$) than it is for the other parameters. The variations of $\xi_d$ with dimer geometry associated with crystal polymorph and anion are $\sim 3\%$, similar to the relative variations of $U^{(v)}_d$ and $V^{(v)}_m$ across the whole data set.
Figure 4.8: Inter-monomer \( V_m^{(v)} \) for various ET dimers. For \( \beta-\text{(ET)}_2X \) crystals, \( V_m^{(v)} = 2.69 \pm 0.13 \) eV and for \( \kappa-\text{(ET)}_2X \) crystals, \( V_m^{(v)} = 2.72 \pm 0.09 \) eV. The mean value is \( V_m^{(v)} = 2.71 \pm 0.10 \) eV. The difference in \( V_m^{(v)} \) between the crystal polymorphs is \( \sim 2\% \). Therefore, \( V_m^{(v)} \), like \( U_d^{(v)} \), does not significantly depend on the geometry associated with crystal polymorph. The effect of ET conformation on the value of \( V_m^{(v)} \) in the crystals \( \beta-\text{(ET)}_2I_3 \) and \( \kappa-\text{(ET)}_2\text{Cu[N(CN)\_2]I} \) is also similar to the effect on \( U_d^{(v)} \). \( V_m^{(v)} \) is lowest when the ET dimer has the staggered-staggered conformation, and rises when either or both ET molecules are eclipsed.
Tight-binding parameterisation of the band structure of quasi-2D layered organic conductors

I have previously discussed instances where the Hubbard model and parameters I have used for ET salts may be improved. The screening correction to the Coulomb parameters is the most notable, because of the sheer magnitude of the adjustment involved. However, the largest remaining body of work to complete the picture of organic conductors represented by Hubbard models is the determination of the hopping parameters, \( t \). Since other research groups are concurrently studying ET salts, I shall briefly introduce an example tight-binding parameterisation for \( \kappa\text{-ET}_2\text{Cu}_2(\text{CN})_3 \), then proceed to apply these techniques to the dmit salts.

5.1 Hopping integrals on tight-binding models of ET salts

In the past, tight-binding parameterisations for ET salts have been accomplished by calculating overlap integrals using an extended Hückel formalism (see, for example, [166]). Once the hopping integrals are known, a band structure could be constructed from the relevant
tight-binding model.

I shall find the hopping integrals essentially in reverse — by fitting a tight-binding model to the DFT band structure. The increased sophistication of a DFT calculation compared to an extended Hückel calculation will improve the accuracy of the resultant band structure, and is consistent with the goal of obtaining the model parameters from first principles calculations.

Kandpal[167, 168] and Nakamura[169] recently independently reported tight-binding parameterisations for \( \kappa \)-ET_2Cu_2(CN)_3. I shall reproduce Kandpal’s result but then, in the interest of novel research, apply the techniques here to materials of the form X[Pd(dmit)_2].

Using the full crystal’s nuclear positions already obtained for \( U \) measurements, I calculated the band structure using the Quantum-Espresso software package.[55] Quantum-Espresso is a plane-wave DFT code, and the calculation was performed with an energy cutoff of 25 Ry for the wavefunctions and 250 Ry for the integration mesh. Again, this calculation was GGA, using the PBE exchange-correlation functional and pseudopotentials available from the Espresso project’s pseudopotential repository. The band structure and tight-binding fit is shown in Figure 5.3.

To obtain the tight-binding model for the crystal, it was necessary to apply the technique introduced by Kandpal.[170] The crystal lattice is shown in Figure 5.1. There is one layer of ET per unit cell, containing four translationally distinct ET monomers. Therefore, I shall construct the Hamiltonian with four sublattices, with appropriate hopping integrals between them.

In order to simplify the Hamiltonian, I shall apply a phase rotation so that each sublattice in the unit cell is in the same position in momentum space. For example, sublattices A and B are related by a \( t_1 \) hopping integral, and the relevant Hamiltonian matrix elements would contain terms like \( t_1 e^{-ik\cdot r_{11}} \), where \( r_{11} \) is the real space displacement vector corresponding to the hop. The phase rotation has the elegant property of making all the \( r_{1i} \) either zero or an integer linear combination of lattice vectors. See Figure (5.2) for a visualisation of this technique.

The Hamiltonian matrix for the k-CN system is
5.1 Hopping integrals on tight-binding models of ET salts

Figure 5.1: The lattice sites of the conducting layer of $\kappa$-ET$_2$Cu$_2$(CN)$_3$ depend on whether the model contains hopping integrals among monomers (left) or dimers (right). In the monomer model, $t_1$ is the intradimer interaction and is typically strongly stabilised by $\pi - \pi$ intermolecular bonding. This makes $t_1$ much larger in magnitude than other $t$ parameters, and separates the four bands of the model into two well-separated pairs. The dimer model would reproduce only the pair of bands nearest the Fermi energy. Note the reduction of parameters, $t' = t_3/2$ and $t = (t_2 + t_4)/2$, required to convert from a monomer model to a dimer model. If $t_1$ is large, little is lost in terms of fitness of the model because $t_1$ is effectively integrated out of the Hamiltonian. Note also the presence of a screw rotation symmetry within the conducting plane. This has the effect of enforcing the symmetry of the two $t$ parameters in the dimer model. This symmetry is absent in the $\beta'$-dmit materials, requiring the relevant dimer model to separate the two $t$ hops into independent parameters. Image from Kandpal et al.[167]

$$\hat{H} = \begin{pmatrix}
\mu & t_1 + t_3 e^{ikb} & t_2(1 + e^{ikb}) & t_4(1 + e^{ikc}) \\
 t_1 + t_3 e^{-ikb} & \mu & t_4(e^{-ikb} + e^{-ik(b-c)}) & t_2(e^{ikc} + e^{ik(-b+c)}) \\
 t_4(1 + e^{-ikc}) & t_4(e^{ikb} + e^{ik(b-c)}) & \mu & t_1 + t_3 e^{ikb} \\
 t_2(1 + e^{-ikb}) & t_2(e^{-ikc} + e^{-ik(-b+c)}) & t_1 + t_3 e^{-ikb} & \mu
\end{pmatrix}.$$ (5.1)

Because the specifics of the crystal structure are parameterised by the vectors $b$ and $c$, this Hamiltonian is actually appropriate for all $\kappa$-type ET crystals with $Z = 1$ (i.e. each ET layer is related by translation to the other layers). In the case that the ET layers are not related only by translation, further sublattices are required to determine the transformed directions of the hops in those layers.
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Tight-binding parameterisation of the band structure of quasi-2D layered
organic conductors

Figure 5.2: (left) A simple unit cell, with two sublattices coloured red and black and two hopping interactions, $t$ and $t'$. A Hamiltonian matrix element would look like $t e^{i k \cdot r_1} + t' e^{i k \cdot r_{1'}}$. (right) The same unit cell, but each sublattice has undergone a phase rotation $e^{i \phi_A}$ and $e^{i \phi_B}$, respectively, such that the $t$ interaction has no phase and the $t'$ interaction has direction $r_{1'} = -a$. The Hamiltonian matrix element is now $t + t' e^{-i k \cdot a}$. The most significant result of this transformation is that the hopping terms no longer depend on the length or direction of the physical hops. All hopping interactions have either $r_1 = 0$ or an integer linear combination of lattice vectors.

I solved this Hamiltonian numerically in Matlab[171] for a set of k-points along the band structure path Kandpal calculated. The DFT band structure and fitted tight-binding model are shown in Figure 5.3. The fitted parameters are $t_1 = 0.18, t_2 = 0.079, t_3 = 0.085,$ and $t_4 = 0.023$. The relationship between the tight-binding parameters are described in Table 5.1, compared to Kandpal’s and Nakamura’s tight-binding parameterisations, as well as a parameterisation of the Heisenberg model. The Heisenberg model describes a lattice of site-local spins with nearest neighbour spin interactions, $J$, which are proportional to $t^2$ and thus the ratio $J'/J$ is comparable to $(t'/t)^2$.[172]

Having shown the effectiveness of this parameterisation process for k-CN, I now apply it to a similar but less studied class of organic conducting materials, dmit.

5.2 Tight-binding parameterisation for the dmit crystals

A similarly interesting organic molecular conductor is the class of materials of the form $X[Y(\text{dmit})_2]_2$, where dmit is 1,3-dithiole-2-thione-4,5-dithiolate. Of particular interest are
Table 5.1: Tight-binding parameters for the tight-binding model of $\kappa$-ET$_2$Cu$_2$(CN)$_3$. The mapping from the monomer model parameter space, $t_{\{1-4\}}$, to the dimer model space, $t$ and $t'$, is $t = (t_2 + t_4)/2$ and $t' = t_3/2$. Zheng’s calculation of $t'$ has a substantial uncertainty range, arising from the uncertainty in the calculation of the spin interaction, $J$. This quantity was calculated from high-temperature series expansions of the magnetic susceptibility, and requires measurement of the temperature corresponding to peak susceptibility, $T_P$. The region of the curve in the vicinity of $T_P$ is unusually flat in $\kappa$-ET$_2$Cu$_2$(CN)$_3$, hence the reported uncertainty. Of particular significance is the quantity $t'/t$, which quantifies the anisotropy of the triangular dimer lattice. There is good agreement among all methods presented here. As $t'/t \to 1$, the lattice becomes more “frustrated”, and such materials exhibit qualitatively different physics to crystals of nearly identical chemical and physical structure. For example, $t'/t = 0.84$ is close to frustration, and the Mott insulating state of $k$-CN has no ordering of spins on neighbouring lattice sites. However, many other $\kappa$-ET crystals exhibit an antiferromagnetic Mott insulating state. A crucial open question of this area is, what amount of frustration is required to drive a crystal from a spin-ordered insulating state to a spin liquid or other qualitatively different insulating state?

<table>
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<th>Nakamura</th>
<th>Zheng</th>
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<td>0.050</td>
<td>0.055</td>
<td>0.050</td>
</tr>
<tr>
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<td>0.044</td>
<td>0.035 – 0.065</td>
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<tr>
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<td>0.84</td>
<td>0.84</td>
<td>0.80</td>
<td>0.85 – 1.15</td>
</tr>
</tbody>
</table>

Figure 5.3: Espresso band structure (blue) and tight-binding fit for a monomer lattice (green) for $\kappa$-ET$_2$Cu$_2$(CN)$_3$. $t'/t = 0.84$ (see Table (5.1). The resultant band structure is an excellent fit to the DFT band structure. This process shall be repeated below for several $\beta'$-dmit materials.
the cases Y = Pd and X = Cs or EtₙMeₙ₋ₙPₙ, where Et is ethyl, Me is methyl and Pₙ is a pnictogen (Group V element, such as N or P). For brevity, dmit materials will be labelled X-n (omitting the -n for Cs).[173] DFT calculations on some M(dmit)₂ materials (where M = Ni, Pd, Pt) have been performed in the past, focusing on orbital interactions of M(dmit)₂ dimers and band structures of, among other materials not studied here, P-0.[174–176] However, these works do not report tight-binding parameterisations for the band structures.

The dmit materials examined here are similar to the ET materials, in that they have a layered cation-anion structure with each layer consisting of dimerised organic units arranged in an anisotropic triangular lattice. Unlike ET salts, the dmit dimers are the anion (acceptor) units.

The similarities between ET and dmit extend to the electronic structure and low temperature phase diagrams, with dmit materials exhibiting temperature and pressure induced metal-insulator transitions, superconductivity, non-antiferromagnetic insulating states, and non-Fermi liquid metals. The literature contains quite accessible recent reviews of current understanding of the dmit materials,[177] and on the unusual electronic states related to the frustration of spins on the lattice.[173]

Briefly, the insulating state of these materials is typically antiferromagnetic, and this behaviour can be observed by measuring the temperature dependence of the spin susceptibility. In an antiferromagnet, the spin susceptibility approximates closely the high-temperature series expansions of the spin-1/2 Heisenberg model, and below the antiferromagnetic transition temperature, $T_N$, the susceptibility falls off sharply[178]. This fall off indicates the growth and spread of regions of antiferromagnetic correlation over the crystal.

Deviation from this behaviour of a sharp fall off of the susceptibility below a threshold temperature $T_N$ is a strong sign of a non-antiferromagnetic state. In the case of spin liquids such as Sb-1, the temperature dependence of the spin susceptibility remains consistent with the spin-1/2 Heisenberg model to very low (tens of mK) temperatures. In the case of the valence bond crystal P-1, the susceptibility features an anomaly from the Heisenberg model (like an antiferromagnet), but since a phase transition still occurs (unlike a spin liquid), the susceptibility anomaly below the transition temperature is qualitatively distinct from the other two cases. This makes the susceptibility a useful probe of the region of the insulating
5.2 Tight-binding parameterisation for the dmit crystals

Figure 5.4: The three basic structures of the dmit materials studied here. (a) The dimer unit has a translation symmetry with every other dimer unit. (b) The dimer has a translation symmetry with other dimers in its layer, but is related to neighbouring layers by a glide plane symmetry. The layers are connected (the smaller lattice sites are in the layer behind the larger) by an interlayer hopping, $t_\perp$. Note this increase of the size of the unit cell in the layering direction decreases the FBZ in the relevant direction in $k$-space. (c) There are two dimers per layer that are not related by a translation symmetry, as well as a screw rotation symmetry between the neighbouring layers.

5.2.1 DFT band structures and tight binding models

Since the physical structure of the dmit materials has the same overall structure of nearly-isolated layers consisting of anisotropic triangular lattices, the same tight-binding techniques used for $\kappa$-ET$_2$Cu$_2$(CN)$_3$ apply here. Among these materials, there are three crystal structures represented, described in Figure (5.4). They are distinguished by their different translation symmetries, and consequently the Hamiltonians must contain a different number of sublattices for each.
The first and simplest structure (see Figure (5.4)) has the simplest Hamiltonian, containing no sublattices and can be determined practically by visual inspection

\[ \hat{H} = 2t_1 \cos(k \cdot a) + 2t_2 \cos(k \cdot b) + 2t_3 \cos(k \cdot (b - a)) + 2t_\perp \cos(k \cdot c) \quad (5.2) \]

One material studied here has this type of structure, N-3. This structure has an antiferromagnetic insulating state. Only one band crosses the Fermi energy in this material.

The second structure type is the most common among the structures I studied. There are eight materials of this type studied here. They are As-0, As-2, Cs, P-0, P-2, Sb-0, Sb-1 and Sb-2.

The Hamiltonian for the second structure type is

\[
\hat{H} = \begin{pmatrix}
\mu - \epsilon + 2[t_1 A + t_2 B_1 + t_3 B_2] & 2t_\perp C \\
2t_\perp C & \mu + \epsilon + 2[t_1 A + t_2 B_2 + t_3 B_1]
\end{pmatrix}
\quad (5.3)
\]

where \( A = \cos(k \cdot a) \), \( B_1 = \cos(k \cdot b) \), \( B_2 = \cos(k \cdot (b - a)) \), \( C = \cos(k \cdot \frac{c}{2}) \), and \( \epsilon \) represents a site energy difference between alternating layers. The symmetries of the crystals studied here imply \( \epsilon = 0 \). Therefore, this parameter will not be considered further. The two sublattices in this Hamiltonian represent alternating layers. Note the rotation symmetry of the crystal results in an exchange of the directions of \( t_2 \) and \( t_3 \) from one layer to the other. The band structure of this Hamiltonian has two bands.

The third structure type is the most complicated, and features sublattices within layers as well as between them. The Hamiltonian for this structure is

\[
\hat{H} = \begin{pmatrix}
\mu - \delta + A & t_2 B + t_3 C & 2t_\perp a D & 2t_\perp b D \\
t_2 B* + t_3 C* & \mu + \delta & 2t_\perp b D & 2t_\perp a D \\
2t_\perp a D & 2t_\perp b D & \mu - \delta + A & t_2 C + t_3 B \\
2t_\perp b D & 2t_\perp a D & t_2 C + t_3 B & \mu + \delta + A
\end{pmatrix}
\quad (5.4)
\]

where \( \delta \) represents a site energy difference between dimers on the same layer, \( A = 2t_1 \cos(k \cdot a) + 2t_4 \cos(k \cdot b) \), \( B = 1 + e^{ik(a+b)} \), \( C = e^{ik a} + e^{ik b} \), and \( D = \cos(k \cdot \frac{c}{2}) \). Two interlayer hopping terms, \( t_\perp a \) and \( t_\perp b \), are present in this crystal type, to distinguish the
hopping between the sublattices in one layer and each sublattice in neighbouring layers.

Only one example of the third structure type is studied here (P-1), although it should be noted that P-1 has a different structure at low temperature. This Hamiltonian produces a four band structure. Since the unit cell of this structure contains the equivalent of two unit cells of the second structure type, the FBZ of these crystals is significantly different. The four band structure of the third type “unfolds” into a two band structure when \( \delta = 0 \), which recovers the intralayer translational symmetry of the tight-binding model. This effect is illustrated in the difference between the band structures of Sb-1 and P-1 (see Figure 5.10).

### 5.2.2 Tight-binding fits for dmit materials

The tight-binding fit for dmit materials follows the procedure for \( \kappa \)-ET₂Cu₂(CN)₃ using a generalised version of the same Matlab code. Table 5.2 contains the parameters of the fit for twelve dmit crystals. The relevant anisotropic triangular lattices considered in the literature use just two parameters, \( t \) and \( t' \), and subsequent analysis of particular Hamiltonians on this lattice explore the ratio \( t'/t \), especially to look for phase transitions, crossovers and quantum critical points. In order to compare my results to existing data, I have averaged the two closest \( t_{[1-3]} \) into \( t_a \), and the extra-anisotropy, \( \Delta t = (t_n - t_m)/2 \), measures the inaccuracy introduced by this simplification. In most cases, this extra-anisotropy is small. The zero energy is the Fermi energy from the DFT calculations, found from solving \( \int_{-\infty}^{E_F} dED(E) = N \), where \( D(E) \) is the density of states and \( N \) is the number of valence electrons per unit cell. This Fermi energy should correspond to half-filling, but I find it is necessary to add an offset to match half-filling within the FBZ. Note however, that the filling was measured in only the conducting plane of the FBZ, but it is unlikely that the filling would be substantially changed from considering \( \mathbf{k} \)-points in the layering direction. The FBZ sampling grid resolution for the filling calculation was 100x100 in the minimal containing rectangle for the FBZ. Therefore, the total number of relevant sample points is marginally less than 10000.

The results show considerable variation in the model parameters for the variety of materials studied. The \( t_{[1-3]} \) range from 0.0180 – 0.0797 eV. \( t_2 \) is the hopping integral in the direction of dimer stacking, i.e. in the same direction as the intradimer hopping parameter.
Table 5.2: The tight-binding parameters for these dmit materials show a variety of model parameter values. All energies are in meV. \( t_a \) is the average of the two closest \( t_{[1−3]} \) and the remaining hopping integral becomes \( t' \), to provide a result \( t'/t_a \) that can be compared to \( t'/t \) values in the literature for some of these materials. (See table 5.3 for this comparison.) The relative difference between the two \( t_{[1−3]} \) is expressed in the quantity \( \Delta t/t_a \), where \( \Delta t \) is the difference between the two \( t_{[1−3]} \). P-1 has two \( t_\perp \) parameters, corresponding to two distinct hopping interactions between the sublattices in one layer and the sublattices in the neighbouring layers.

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<th>( t_2 )</th>
<th>( t_3 )</th>
<th>( t_a )</th>
<th>( t'/t_a )</th>
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<td>48.8</td>
<td>45.1</td>
<td>47.0</td>
<td>0.72</td>
<td>4.0</td>
<td>5</td>
<td>-215</td>
</tr>
</tbody>
</table>

would be were the model to use monomers as lattice sites rather than dimers. However, while the overlap between molecules in a dimer is nearly total, the dimers have substantially less overlap with neighbouring dimers in the same direction as the dimer stacking. This also occurs in the \( \beta-\text{ET}_2\text{X} \) crystals. This reduces the strength of the interdimer hopping in this direction such that it is comparable to the hopping integrals in the other two in-plane directions. There are two materials (P-0 and P-2) with relatively large extra-anisotropy, 10%. In other cases, the extra-anisotropy ranges from 0 – 5%. Therefore, the reduction in the number of parameters with the use of \( t_a \) is a valid means of comparison with data that uses the \((t, t')\) parameter space.

The interlayer hopping integral, \( t_\perp \), varies from \(< 0.0001\) eV in several cases to \(0.0085\) eV in the case of Cs at room temperature. This \( t_\perp \) is quite significant, approximately 20% of the intralayer \( ts \). This may even be enough to destroy the quasi-2D character of the dmit materials, although it is important to point out that Cs undergoes a structural change as it cools to the temperature region of the insulating state and the low temperature structure may have a lower \( t_\perp \). The other materials have \( t_\perp/t_a \) in the range of \(0 – 3\%\), justifying the
5.2 Tight-binding parameterisation for the dmit crystals

Figure 5.5: The DFT band structure (black dots) and tight-binding fit (green line) for N-3 are quite distinct from that of other materials presented below, as is expected from the unique (among this data set) crystal structure. This is the only structure with one band crossing the Fermi energy. The tight-binding parameterisation of N-3 has the greatest anisotropy of the materials studied in this work, $t'/t = 0.33$. This has the most effect on the band structure near the Y point. The Fermi surface of N-3 closely approaches the FBZ boundary, indicating the material has a near quasi-1D character.

The figures below show the DFT band structures for the materials studied and the subsequent tight-binding fits. The overall fit is quite high quality, and is optimised for accurate band widths (i.e. accurate at the high-symmetry points). While this is suitable for calculating tight-binding parameters, the model fares less well towards the middle of the bands’ energy ranges, in some cases near the Fermi energy at half filling. Therefore, the Fermi surfaces and the derived calculations of the band filling and associated $\mu_{1/2}$ will reflect this disagreement. This effect is not qualitative. The fit quality can be improved, either by adjusting the weights of the fit in favour of the energy range of interest, or by introducing more parameters, e.g. a monomer model.

5.2.3 Spin liquids and valence bond crystals

Two of the dmit materials studied here have particularly unusual physics. Both materials, like the others, have insulating states and a Mott transition. However, the insulating state
Figure 5.6: The DFT band structure and tight-binding fits for As-0 (a), As-2 (b) and Cs (c). Note that the Cs band structure is for a room temperature crystal structure. The band structures and Fermi surfaces are marginally different among these materials. $t'/t = 1.42$ for As-0, compared to 1.26 for As-2 and 0.93 for Cs. The fit for Cs is relatively poor, but the poor fit is localised to features not near $E_F$. The fit is reasonably good near $E_F$, so the associated Fermi surfaces are not significantly affected. The bands of As-2 feature avoided crossings, resulting in the tilted shape of the Fermi surface. The crossover points are visible in the band structure, in the vicinity of V and X. These crossovers are absent in the other two band structures.
5.2 Tight-binding parameterisation for the dmit crystals

Figure 5.7: The DFT band structure and tight-binding fits for P-0 (a) and P-2 (b & c). Note that the P-2 band structures are from crystal structures measured at room temperature. At low temperatures, P-2 adopts the third type of crystal structure, similar to P-1, and most likely undergoes significant changes to the tight-binding parameters. All three of these structures have avoided band crossings, evidenced by the crossing Fermi surfaces. P-0 actually has one band crossing the FBZ boundary in the Y direction, indicating a relatively strong quasi-1D character. $t'/t = 1.48$ for P-0, which is the highest $t'/t$ of the materials studied.
Tight-binding parameterisation of the band structure of quasi-2D layered organic conductors

Table 5.3: Several of the dmit compounds exhibit a temperature-driven metal-antiferromagnetic insulator transition at the listed temperatures. There is substantial disagreement between my tight-binding parameters and the ones Shimizu used, and this is reflected in the less simple relationship between $t'/t$ and the transition temperature $T$ (see Figure (5.11). There are two P-2 structures studied in this work, which is why two $t'/t$ values are listed.

<table>
<thead>
<tr>
<th>Cation</th>
<th>T</th>
<th>$t'/t$ (Shimizu)</th>
<th>$t'/t$ (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-0</td>
<td>42</td>
<td>0.59</td>
<td>1.48</td>
</tr>
<tr>
<td>As-0</td>
<td>35</td>
<td>0.67</td>
<td>1.42</td>
</tr>
<tr>
<td>P-2</td>
<td>17</td>
<td>0.83</td>
<td>1.35, 0.75</td>
</tr>
<tr>
<td>As-2</td>
<td>16</td>
<td>0.82</td>
<td>1.26</td>
</tr>
<tr>
<td>Sb-0</td>
<td>16</td>
<td>0.85</td>
<td>1.23</td>
</tr>
<tr>
<td>Sb-1</td>
<td>0</td>
<td>0.92</td>
<td>0.79</td>
</tr>
<tr>
<td>P-1</td>
<td>25</td>
<td>1.03</td>
<td>0.87</td>
</tr>
</tbody>
</table>

is not antiferromagnetic in Sb-1 and P-1.[173, 177]

Sb-1 is a spin liquid, similar to $\kappa$-ET$_2$Cu$_2$(CN)$_3$. This has two important implications. First, the appearance of such an unusual state in both ET and dmit materials, highlights the point that the two materials exhibit very similar physics. Second, this means the tight-binding parameters obtained for Sb-1 can be compared to the parameters for the other materials, ultimately toward an effort to establish a phase diagram in the tight-binding parameter space that can differentiate between these different insulating states. Using my data, I have constructed an analogous graph similar to Shimizu’s Hückel calculations,[186] showing the transition temperatures against my calculated $t'/t$ values (see Figure (5.11)).

These materials are all examples of quantum critical systems.[187] Quantum critical systems are those which may undergo a phase transition due to fluctuations associated with Heisenberg’s uncertainty principle. This allows phase transitions even at zero temperature, where the quantum fluctuations result in atomic and electronic motion even in the absence of thermal energy available for nuclear motion. Quantum criticality can be probed by the measuring the temperature dependence of bulk quantities sensitive to these fluctuations, such as the specific heat capacity or resistivity. These materials are highly studied research targets, because the qualitative implications of quantum criticality provide new insights into the nature of the phases involved, and ultimately the general nature of condensed matter.

The insulating state of P-1 is different again, known as a valence bond crystal (VBC).
A VBC can be thought of as a state in which the spins on each lattice site form singlet pairs with neighbouring lattice sites in a way that still possesses translational symmetry, though not the same translational symmetry as the crystal lattice. The band structure and Fermi surface of P-1 as calculated both directly from DFT and from the parameterised tight-binding model are shown in Figure (5.10).

There is no obvious way to relate the tight-binding parameters to these various insulating states. Sb-1 has a $t'/t_a = 0.79$, but the antiferromagnet P-2 has $t'/t_a = 0.75$. However, that P-2 structure is at room temperature, and has a different structure at low temperature. P-1 has a $t'/t_a = 0.87$, also near the value for Sb-1. Unless these structures are indeed situated close to either side of a phase transition, it is probable that more parameters are required to characterise and differentiate these states. However, based on the transferability of $U_d^{(v)}$ for the ET salts, it is likely that the same considerations for improving the predictive power of effective low energy Hamiltonians in those materials applies to the dmit salts as well.
Figure 5.8: The DFT band structure and tight-binding fits for Sb-0 (a) and Sb-2 (b). Note that the Sb-2 band structure is for a room temperature crystal structure. At low temperature, Sb-2 adopts the same type of crystal structure as P-1 and most likely undergoes significant changes to the tight-binding parameters. Both materials have avoided crossings, with Fermi surfaces slanted towards Y (Sb-0) and M (Sb-2). It is interesting to note that these two materials are substantially above (Sb-0, $t'/t = 1.23$) and below (Sb-2, $t'/t = 0.72$) the frustrated region, but their band structures and Fermi surfaces are more similar to each other than most other materials compared here in this way.
Figure 5.9: The band structure and Fermi surface (a) of Sb-1 are quite similar to the other type 2 dmit materials studied here. However, the separation between the bands is quite small, especially in the M-V-Y region of the band structure, where most of the dmit materials have some asymmetric features and more rapidly varying energy differences between the bands at \( k \)-points in that region. This results in a Fermi surface with avoided crossings, like several of the other materials, but with a substantially smaller separation between the Fermi surfaces in \( k \)-space. Doubling the unit cell in the conducting plane yields a folded down band structure and Fermi surface (b), due to the reduced FBZ. This downfolded band structure allows a more direct comparison between the electronic structure of Sb-1 and that of P-1 (see Figure (5.10)) and \( \kappa\text{-ET}_2\text{Cu}_2(\text{CN})_3 \) (see Figure (5.3)). Of particular note is the emergence of secondary orbits (red and black lines) formed from the edge of the downfolded Fermi surface. These regions actually represent a third and fourth band crossing the Fermi energy, but only in the region of \( k \)-space near Z.
Tight-binding parameterisation of the band structure of quasi-2D layered organic conductors

Figure 5.10: The band structure of P-1 (a) has an unusual feature — a third band crossing the Fermi energy due to the downfolding of the Fermi surface onto this smaller FBZ. The red band is 99.82% full, which slightly affects the filling of the other two bands (52.7% (green) and 47.4% (blue)). The model Fermi surface (b) and DFT Fermi surface (c) show that the shape of the bands is due to the folding down of the FBZ into the smaller space as the real space unit cell is enlarged. The band structure fit captures the band widths and several features well, but there is some inaccuracy of the model fit in the region near the Fermi energy. This is evidenced by the distinctions between the model’s Fermi surface and the one calculated in DFT from a 2D sweep of the FBZ in the conducting plane. In particular, the model band structure does not capture the slant of the Fermi surface in the M direction, as evidenced by the poor fit in the M-X region of the band structure. The addition of more hopping parameters, perhaps through the use of a monomer model, could improve the fit in this situation and more accurately reproduce the DFT result. Note the similarity between this band structure, Sb-1 (Figure 5.9) and $\kappa$-ET$_2$Cu$_2$(CN)$_3$ (Figure 5.3)).
5.2 Tight-binding parameterisation for the dmit crystals

Figure 5.11: (Left) The relationship between $t'/t$ and the transition temperature to the antiferromagnetic insulating state (a-f), the absence of a phase transition as low as several mK (g), and the transition of P-1 to the valence bond crystal state (h), as collected by Shimizu et al. seems very straightforward from model parameterisations using Hückel methods (left). However, my parameterisation of the tight-binding model from the DFT band structure (right) shows that the relationship is more complicated. The antiferromagnets (a-f on Shimizu’s graph and the black circles on mine) are present in my graph in the same region of parameter space as the spin liquid Sb-1 and the valence bond crystal P-1 (g and h on Shimizu’s graph, respectively). $t'/t$ alone is insufficient to characterise their different insulating states, other phenomena besides the hopping integrals influence both the low temperature physics of the materials and a more sophisticated Hamiltonian would consider more of these variables.
Summary and outlook

The materials I have studied here collectively possess a variety of the phases available to the quasi-2D layered organic molecular conductors, and to strongly-correlated materials in general. The use of low energy effective Hamiltonians to probe these materials from first-principles computational techniques is remarkably useful and informative. Almost counter-intuitively, the DFT techniques as I have used them cannot recover directly the qualitative nature of these materials. Nevertheless, the individual parameters of the models may be explored in isolation under cluster conditions for site-local parameters, and periodic conditions for delocalised parameters, to inform the effective low energy Hamiltonians.

The site-local parameters of the one and two site Hubbard models on the ET salts studied are quite uniform, indicating the role delocalised parameters play in the characterisation of the variety of phases available to these systems. The DFT results disagreed with earlier Hückel calculations, highlighting the importance of considering electron-electron interactions, even approximately. This work is part of a larger effort to parameterise these models on these materials. In particular, concurrent work from other research groups to calculate the hopping parameters and screening corrections to the Coulomb energy, when considered with these results provides a more complete first-principles characterisation of the ET salts. Furthermore, the eventual complete parameterisation of Hubbard models on an anisotropic triangular lattice for these materials will inform efforts to refine the models to more correctly represent these materials, and provide target regions of parameter space for efforts to solve these models analytically or through approximate methods.
A benefit to the uniformity of the site-local parameters is that the effect of disorder is significant, and this was exploited to recover in one case the quantitative effect of disorder on the $T_C$ of superconducting state. The natural extension of this work is to use this parameterisation to predict the effect of disorder on other observables in other phases, such as the spin susceptibility of the insulating states.

The tight-binding parameterisation of the dmit salts show an interesting variety of parameter values for the materials studied. Those materials whose insulating states are expected to correlate with frustration in the tight-binding parameters are indeed found to have parameter values in the expected region. It is only recently that tight-binding parameters in the ET salts were found from a DFT band structure, rather than finding the tight-binding parameters from overlap integrals and deriving the band structure from the model.

The differences between the results of those two techniques are as large for $t$ parameters in the dmit salts as they are for $U$ parameters in the ET salts, upon comparison of this application of a DFT tight-binding parameterisation to the dmit salts to extant Hückel calculations in the literature. The calculation of the site-local parameters of the Hubbard model for the dmit materials is the natural next step of this overall research effort, and will eventually allow direct theoretical comparison between the ET and dmit salts and their similar phase diagrams through their similar and relatable model Hamiltonians.
References

[58] B. J. Powell, M. R. Pederson, and
References

[62] A. Girlando, M. Masino, G. Viscen-


