Orthogonalising Pseudo-Potentials in electronic structure calculations

J. Mitroy, G.G. Ryzhikh

Atomic and Molecular Physics Laboratories, ANU, Canberra, ACT 0200, Australia
Faculty of Science, Northern Territory University, Darwin, NT 0909, Australia

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Abstract

An investigation of the Orthogonalising Pseudo-Potential (OPP) introduced by Kukulin and Krasnopolsky is made with the emphasis on its numerical application. The OPP method is a projection operator technique to remove unwanted states from a many body calculation. An analysis of a model two level system was used to deduce the basic properties of the spectrum of the projected Hamiltonian. Detailed plots of the atomic properties of Na, Na\(^+\), Na\(^-\), and NaPs were made as a function of the strength of the OPP to exhibit the operation of the OPP procedure for some complicated many-body systems. An improved wave function for the NaPs ground state was generated as a byproduct of this investigation. The current best estimates of the NaPs binding energy and annihilation rate are 0.008009 Hartree and \(2.072 \times 10^{10}\) s\(^{-1}\), respectively. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the major difficulties of any electronic structure calculation is the fact that the antisymmetric nature of the wave function gives rise to two features that tend to complicate matters. These are the exchange interaction and the Pauli principle. The matrix elements of exchange type interactions are generally more complicated and more difficult to evaluate than those of the direct interaction. While this is an important concern, the present article does not discuss this issue. The present manuscript is concerned with the Pauli principle which states that two electrons cannot simultaneously occupy a state with the same quantum numbers. One of the easiest ways of enforcing the Pauli principle in a calculation is to use a single particle basis constructed from an orthonormal set of states. This is not a necessary condition and it is possible to use a basis set that is not orthonormal provided one is prepared to handle many body matrix elements that can be very complicated and to solve the general (instead of ordinary) eigenvalue problem.

One of the standard issues that arises in the field of electronic structure calculations is how to treat the core of a system that contains a large number of electrons. A number of frozen core and model potential schemes have been developed and used to attack these systems [1–3]. Besides the problem of defining the core potential, it is also necessary to ensure that the valence electrons do not collapse into the core orbitals that are already occupied.

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There are variety of techniques to accomplish this task. The Lagrange multipliers in Hartree–Fock calculations can be used to ensure orthogonality with the core [4,5]. In more sophisticated calculations, the use of an underlying orthogonal single particle basis makes it easy to satisfy the Pauli principle. Lagrange multiplier techniques are also used in electron scattering calculations using the R-matrix approach [6]. Finally, one can construct projection operators that will ensure the wave function is orthogonal to the core orbitals.

However, there are circumstances where the standard procedures are difficult to apply. In pseudo-potential calculations it is common to modify the Hamiltonian so that the problem no longer exists. A pseudo-potential can be constructed that is repulsive (rather than attractive) in the inner region of the atom (or molecule). The spectrum of a node-less pseudo-potential has no low lying eigenstates corresponding to occupied levels and therefore the problem is eliminated. However, the pseudo-potential will give wave functions with an incorrect number of nodes, a result which at the least is somewhat unaesthetic [7].

The present manuscript discusses one particular method of enforcing the Pauli principle in an electronic structure calculation. The Orthogonalised pseudo-potential (OPP) method was first introduced by Krasnopolsky and Kukulin [8,9] and has the properties that it is simple to comprehend, is easy to apply and also produces wave functions with the correct nodal structure. Despite these desirable properties, the method has received only intermittent usage in the field of nuclear physics over the years and does not seem to be widely appreciated.

In the area of quantum chemistry, Bonifacic and co-workers have developed a model potential method [3,10] that is related to the OPP and used it to determine the structure of molecules containing heavy atoms. The particular version of the OPP developed by Bonifacic and Huzinaga has widespread use in quantum chemistry and related areas [3,11–14].

Despite the use of the OPP procedure in a number of calculations [15–18], it has not been subjected to a comprehensive numerical investigation. In the present manuscript, an analytic treatment of the OPP procedure is performed for a simple two level system. Following this, we make a numerical examination of the behaviour of the OPP procedure in the context of some complicated many-body systems, the ground states of Na, the sodium anion (Na$^-$), positronic sodium Na$^+$ and sodium positride (NaPs).

2. The orthogonalised pseudo-potential method

The basic philosophy of the OPP as put forward by Kukulin and Krasnopolsky [8,9] is to add a penalty function to the Hamiltonian to enforce orthogonality with those orbitals to be excluded from the active space. The penalty function added to the Hamiltonian is the operator

$$\lambda \hat{P} = \sum_i \lambda \langle \psi_i | \psi_i \rangle,$$  

(1)

where $\lambda \hat{P}$ is constructed by summing over the single particle orbitals to be excluded from the calculation (typically the orbitals occupied by the core electrons). Provided $\lambda$ is positive, the expectation value of this operator is always positive. When $\lambda$ is chosen to be a sufficiently large number, any component of the wave function which is not orthogonal to the core will tend to increase the energy. Therefore, any variational method which seeks to minimise the energy will attempt to construct a wave function with a minimum overlap with the core orbitals.

The operation of the OPP is first discussed for a simple two level atom, and then the operation of the OPP is examined for the ground states of Na, Na$^-$, Na$^+$ and NaPs.

2.1. One body case

Consider an 1-body Schrödinger equation given by

$$\hat{H} |\psi\rangle = E |\psi\rangle.$$  

(2)
Let the set \{Φ_i\} be the complete set of solutions of this equation with energies \{E_i\}. Suppose it is wished to solve the Schrödinger equation but exclude certain states from the manifold of solutions. The traditional way to do this is to use a projection operator.

The projection operator \( \hat{Q}_0 \) to exclude the ground state |Φ_0\rangle from the set of solutions is defined

\[
\hat{Q}_0 = 1 - \hat{P}_0 = 1 - |Φ_0\rangle\langle Φ_0|.
\]

The explicit inclusion of this projection operator into the Schrödinger equation gives

\[
\hat{Q}_0 \hat{H} \hat{Q}_0 |ψ\rangle = E |ψ\rangle.
\]

The first excited state of \( \hat{H} \) is now the ground state of this modified Hamiltonian (the projection operator has shifted the energy of \(|Φ_0\rangle\) to zero). The ground state has effectively been removed from the spectrum at the expense of working with a more complicated Hamiltonian with additional nonlocal operators.

In a lot of circumstances this projection operator technique is easy to apply and does not increase the computational labour to any great extent. However, there are a number of circumstances where the use of Eq. (4) is impractical and anything that can be done to simplify the situation is desirable. The operator \( \lambda \hat{P}_0 \) can act as a projection operator for the state |Φ_0\rangle when it is added to the Hamiltonian and \( \lambda \) is chosen appropriately. The modified Schrödinger equation is

\[
(\hat{H} + \lambda \hat{P}_0) |ψ\rangle = E |ψ\rangle.
\]

This equation has the same eigenvalues and eigenvectors as Eq. (4) with one exception. The energy of the eigenstate |Φ_0\rangle is shifted to \( E_0 + \lambda \) while the energies of the other eigenstates remain unchanged. Provided \( \lambda > |E_0 - E_1| \), the lowest energy state of the modified Hamiltonian will be \( E_1 \). If \( \lambda \) is greater than \( |E_0| \) then the energy of |Φ_0\rangle is shifted into the continuum. The expectation value of \( \hat{P}_0 \) for the lowest energy eigenstate is a step function

\[
\langle \hat{P}_0 \rangle = \begin{cases} 1; & \lambda < |E_0 - E_1|, \\ 0; & \lambda > |E_0 - E_1|. \end{cases}
\]

In most of the situations that arise in calculations on real systems, the states to be excluded will not be exact eigenstates of \( \hat{H} \) (however they are good approximations to eigenstates). When the projected state is not an eigenstate of \( \hat{H} \), the \( \lambda \) dependence of \( \langle \hat{P}_0 \rangle \) becomes more complicated. Insight into the behaviour of the OPP for this more general problem can be gained by investigating a model two level system.

Let the state we wish to exclude be written as a linear combination of the two lowest eigenstates of \( \hat{H} \), viz.

\[
|Ω\rangle = α|Φ_0\rangle + β|Φ_1\rangle.
\]

In this expression \( α^2 + β^2 = 1 \). Applying the projection operator, the lowest energy eigenvalue of \( \hat{Q}_{Ω} \hat{H} \hat{Q}_{Ω} \) is \( β^2 E_0 + α^2 E_1 \) and while the eigenstate is \( |ψ\rangle = β|Φ_0\rangle - α|Φ_1\rangle \). The energy of the state |Ω\rangle is shifted to zero by the inclusion of the projection operators.

Diagonalising the OPP Hamiltonian,

\[
(\hat{H} + \lambda \hat{P}_{Ω}) = (\hat{H} + \lambda,|Ω\rangle\langle Ω|),
\]

yields an expression for the eigenvalues that depends on \( λ \), viz.

\[
E_{Ωi} = \frac{1}{2} \left( λ + E_0 + E_1 \pm \sqrt{(λ + E_0 + E_1)^2 - 4E_0E_1 - 4λ(β^2 E_0 + α^2 E_1)} \right).
\]

When \( i \) in \( E_{Ωi} \) (and |ψ_i\rangle) is zero the negative sign is used, and when \( i = 1 \), the positive sign in front of the square root is used. The eigenvectors are

\[
|ψ_i\rangle = \frac{1}{X_i} \{ C_+|Φ_0\rangle + |Φ_1\rangle \},
\]
Fig. 1. Variation of the energy eigenvalues of the 2 state model defined by Eq. (8) as a function of $\lambda$.

Fig. 2. Variation of $\langle \hat{P}_2 \rangle_0$ for the 2 state model as a function of $\lambda$ (in Hartree). Curves are shown for $\beta = 10^{-1}$, $\beta = 10^{-2}$, $\beta = 10^{-3}$, and $\beta = 10^{-4}$.

where

$$C_{\pm} = \frac{1}{2\lambda\alpha\beta} \left( \lambda \left( \alpha^2 - \beta^2 \right) + E_0 - E_1 \pm \sqrt{\left( \lambda + E_0 + E_1 \right)^2 - 4E_0E_1 - 4\lambda(\beta^2E_0 + \alpha^2E_1)} \right)$$  \hspace{1cm} (11)

and the normalisation factor $X_{\pm}$ is

$$X_{\pm} = \sqrt{1 + C_{\pm}^2}.$$  \hspace{1cm} (12)

The energy eigenvalues $E_{20}$ and $E_{21}$ are now functions of $\lambda$ and their behaviour as a function of $\lambda$ is shown in Fig. 1. The curves were generated for a variety of values of $\beta$ with $E_0 = -40$ and $E_1 = -0.2$. The energy of the eigenstate which is dominated by the $|\Omega\rangle$ configuration is close to a linear function of $\lambda$ with the degree of linearity increasing as $\beta$ is decreased. The critical value of $\lambda$ that denotes the cross-over point for the two eigenvalues is once again given by $\lambda_{\text{crit}} = |E_0 - E_1|$.

The composition of the lowest energy eigenstate of Eq. (8) is best determined by plotting the behaviour of $\langle \hat{P}_2 \rangle_0$ as a function of $\lambda$ and this was done in Fig. 2. The most notable feature of Fig. 2 is the abrupt decrease in $\langle \hat{P}_2 \rangle_0$ at $\lambda_{\text{crit}}$. The eigenstate is dominated by the $|\Omega\rangle$ configuration when $\lambda < \lambda_{\text{crit}}$, while for $\lambda > \lambda_{\text{crit}}$ the
configuration has been largely expunged from the eigenstate. The functional dependence of $\langle \hat{P}_\Omega \rangle_0$ versus $\lambda$ increasingly resembles a step function as $\beta$ decreases.

Although there is an abrupt change in the composition of the lowest eigenvector at $\lambda_{\text{crit}}$, the eigenvectors still have some dependence on $\lambda$ for $\lambda > \lambda_{\text{crit}}$. The extent to which this has an influence on the energy and wave function is best seen by the use of a $1/\lambda$ expansion. In the limit of large $\lambda$, the lowest eigenvalue of Eq. (8) tends to that of $\tilde{Q}_\Omega \tilde{H} \tilde{Q}_\Omega$ from below with a correction term of $O(1/\lambda)$. To be specific,

$$E_{\Omega 0} = \beta^2 E_0 + \alpha^2 E_1 - \alpha^2 \beta^2 (E_0 - E_1)^2 / \lambda,$$
$$E_{\Omega 1} = \lambda + \alpha^2 E_0 + \beta^2 E_1 + \alpha^2 / \lambda = 2 E_0. \quad (13)$$

The eigenvectors can be written as a $1/\lambda$ expansion,

$$|\Psi_0\rangle = \beta (1 - \alpha^2 (E_0 - E_1)/\lambda)|\Phi_0\rangle - \alpha (1 + \beta^2 (E_0 - E_1)/\lambda)|\Phi_1\rangle,$$
$$|\Psi_1\rangle = \alpha (1 + \beta^2 (E_0 - E_1)/\lambda)|\Phi_0\rangle + \beta (1 - \alpha^2 (E_0 - E_1)/\lambda)|\Phi_1\rangle. \quad (14)$$

The factor $\beta^2 (E_0 - E_1)^2$ multiplying the $O(1/\lambda)$ correction to the energy largely determines the extent to which $E_{\Omega 0}$ underestimates the true energy since $\alpha^2 \approx 1$. The difference between $E_{\Omega 0}$ and the exact solution of Eq. (8),

$$\delta E_{\Omega 0} = |E_{\Omega 0} - (\beta^2 E_0 + \alpha^2 E_1)|,$$

is shown in Fig. 3. The tendency for $\delta E_{\Omega 0}$ to decrease as $\beta$ decreases is readily apparent.

The expectation values of the OPP potential, $\langle \lambda \hat{P}_\Omega \rangle$ accurate to $O(1/\lambda^2)$, are

$$\langle \hat{P}_\Omega \rangle_0 = \alpha^2 \beta^2 (E_0 - E_1)^2 / \lambda^2,$$
$$\langle \hat{P}_\Omega \rangle_1 = 1 - \alpha^2 \beta^2 (E_0 - E_1)^2 / \lambda^2. \quad (16)$$

These expectation values determine the extent to which the wave function is contaminated by the unwanted solution and the $O(1/\lambda^2)$ decrease of $\langle \hat{P}_\Omega \rangle_0$ means that the unwanted component of the wave function is decreasing as $O(1/\lambda)$. The expectation value of $\langle \lambda \hat{P}_\Omega \rangle_2$ is equal in magnitude to the $O(1/\lambda)$ correction for $E_{\Omega 0}$. Therefore if $\langle \lambda \hat{P}_\Omega \rangle_0$ is added to $E_{\Omega 0}$, the revised estimate for the energy is correct to $O(1/\lambda^2)$. This result does not seem to be useful in the context of a real many-body calculation since the results obtained in the next section indicate that numerical rather than analytic considerations seem to limit the accuracy of wave functions computed with the OPP Hamiltonian.
2.2. Test calculations for Na, Na\textsuperscript{−}, Nae\textsuperscript{+} and NaPs

In this section the results of numerical investigations carried out on a number of systems based on the sodium atom are presented. The systems investigated were neutral sodium (Na), the sodium anion (Na\textsuperscript{−}), positronic sodium (Nae\textsuperscript{+}) and sodium positride (NaPs). The aim of this investigation was to examine the dependence of the binding energy and other atomic properties on \( \lambda \) in the context of a complicated many body calculation. Previous calculations on the Nae\textsuperscript{+} and NaPs ground states (and other positron binding systems) were performed with the OPP Hamiltonian [15–17]. These positron binding systems are all characterised by exceptionally strong electron–positron correlations which almost mandate the use of trial wave functions with \( r_{ij} \) correlation factors.

The evaluation of the matrix elements of the projected Hamiltonian \( O_{ij} \) is a difficult proposition for trial wave functions containing \( r_{ij} \) coordinates and was avoided by using the OPP Hamiltonian.

The Hamiltonian used for the present calculations has been discussed previously [17] so only a brief description is given here. The inner electrons in the 1s, 2s and 2p shells were frozen and represented by a Hartree–Fock wave function. The Hartree–Fock single particle orbitals were expanded as a linear combination of Gaussian Type Orbitals. The Hartree–Fock 1s, 2s and 2p orbitals were used to construct the projection operator acting on the 2 valence electrons. In addition, one and two body polarisation potentials act on the active electrons and the positron (the Gaussian expansion of the polarisation potential is slightly different from that previously given in [17]).

The wave functions for the active particles were written as a linear combination of explicitly correlated Gaussians and the optimum exponents were determined by the stochastic variational method [17,19–21]. The OPP parameter, \( \lambda \), was set to 10\(^6\) Hartree when the nonlinear exponents of the wave functions were being optimised. A linear combination of 30 ECGs was used to describe the Na atom while the Na\textsuperscript{−} wave function was constructed from a linear combination of 260 ECGs. The positronic sodium wave function was constructed from 250 ECGs. For all practical purposes these wave functions were almost identical to those reported in [17]. Two different basis sets were used for NaPs. One wave function was constructed from a linear combination of 600 ECGs and was similar in quality to the wave function reported in [16]. The other wave function had a basis of dimension 870 and is the best quality wave function so far constructed for the NaPs system. The two different basis sets for NaPs are referred to as the NaPs(600) basis set and the NaPs(870) basis set.

Some plots of energy versus \( \lambda \) for Na and NaPs are shown in Fig. 4. Plots for Nae\textsuperscript{+} and Na\textsuperscript{−} were not given since they would just clutter the figure and not give any extra information. The plot of the Na energy versus \( \lambda \) is certainly reminiscent of Fig. 1. At \( \lambda = 0 \), the electron is occupying the 1s core orbital. For values of \( \lambda \) less than 40.4 Hartree, the binding energy is a linear function of \( \lambda \), i.e. \( E_0(\lambda) = A + \lambda \). At values of \( \lambda > \lambda_{\text{crit}} \) = 40.4 Hartree, the binding energy was more or less constant at \( -0.188391 \) Hartree. The \( E \) versus \( \lambda \) curve for NaPs is different from the Na curve, but the differences occur because NaPs has two active electrons. At \( \lambda = 0 \), both electrons have collapsed into the 1s core orbital. (The energy of the NaPs wave function at \( \lambda = 0 \) is not equal to twice the Na energy because of the Coulomb repulsion between the two electrons.) At small values of \( \lambda \), the lowest energy eigenvalue is a linear function of the form, \( E_0(\lambda) = A + 2\lambda \). The equation defining the curve changes to \( B + \lambda \) when the first electron is forced out of the 1s orbital by the increasing value of \( \lambda \). The second electron is expelled from the 1s orbital after a further small increase in \( \lambda \). That the two electrons are forced out of the 1s orbital by the OPP potential at different values of \( \lambda \) is a consequence of the mutual Coulomb repulsion between the two electrons. With two different critical values of \( \lambda \) there is some ambiguity in defining \( \lambda_{\text{crit}} \). In order to eliminate this ambiguity we define \( \lambda_{\text{crit}} \) for those systems that have two active electrons (e.g. Na\textsuperscript{−} and NaPs) to denote the point at which both electrons have been removed from the 1s shell. The value of \( \lambda_{\text{crit}} \) can be related to the Koopman energies of the Hartree–Fock wave function used to define the core orbitals. While exact agreement with the Koopman energy is not expected, the Koopman energy should give a reasonable estimate of \( \lambda_{\text{crit}} \). The Koopman energy, \( \epsilon_{1s} \), for the Na ground state is \(-40.47\) Hartree, while \( \lambda_{\text{crit}} \) is 40.57 Hartree for Na and \( \lambda_{\text{crit}} \) is 40.55 Hartree for NaPs. This linear behaviour of energy for \( \lambda < \lambda_{\text{crit}} \) has also been seen in calculations of 2-nucleon and 3-nucleon binding energies from NN potentials derived from a quark model of the nucleus [18].
Fig. 4. The Na and NaPs binding energies with respect to the Na$^+$ core are plotted as a function of $\lambda$ (in Hartree). The solid curve was computed from the NaPs(870) wave function while the short dashed curve shows the Na binding energy.

Fig. 5. The expectation value $\langle \hat{P} \rangle$ for the Na, Na$^-$, Nae$^+$, NaPs(600) and NaPs(870) ground state wave functions as a function of $\lambda$ (in Hartree).

The plots of $\langle \hat{P} \rangle$ versus $\lambda$ shown in Fig. 5 are also reminiscent of the behaviour of the model problem. All the $\langle \hat{P} \rangle$ versus $\lambda$ curves experience abrupt drops in $\langle \hat{P} \rangle$ at $\lambda_{\text{crit}}$. For example, $\langle \hat{P} \rangle$ changes from 0.9987 to $9.512 \times 10^{-4}$ when $\lambda$ changes from 40.5 to 40.6 Hartree for the NaPs(870) wave function. The Na$^-$ and NaPs curves have a small ledge in the step function which signifies the points where each electron is forced out of the core by increasing the size of $\lambda$. The plot for neutral sodium, Na, is almost an exact mimic of the two level model since $\langle \hat{P} \rangle$ falls off as $1/\lambda^2$ for $\lambda > 100$ Hartree. The rate at which $\langle \hat{P} \rangle$ decreases as a function of $\lambda$ depends on the complexity of the system with the simplest systems having the most rapid decrease. Nae$^+$ represents a simpler system than Na$^-$ from the viewpoint of the OPP method since it only has one electron to exclude from the core. The NaPs system is obviously the most complicated and has the biggest values of $\langle \hat{P} \rangle$ at high $\lambda$. That the Nae$^+$, Na$^-$ and NaPs systems do not have the expected $O(1/\lambda^2)$ decrease in $\langle \hat{P} \rangle$ for $\lambda > \lambda_{\text{crit}}$ is probably an inevitable consequence of doing a calculation with a basis of finite dimension.

The problems inherent with finite basis calculations are also apparent in Fig. 6 where $\langle \lambda \hat{P} \rangle$ is plotted as a function of $\lambda$ for all the systems under consideration. One feature that is common for Na$^-$, Nae$^+$ and NaPs is the increase in $\langle \lambda \hat{P} \rangle$ for values of $\lambda$ greater than $10^3$ Hartree. This indicates that the basis sets lack the flexibility to decrease
The expectation value $\langle \hat{P} \rangle$ beyond a specific minimum value. This effect can also be noticed in Fig. 5 where $\langle \hat{P} \rangle$ has stopped decreasing and plateaued at a constant for the NaPs(600) and NaPs(870) wave functions while the Na$^-$ and Nae$^+$ curves are tending towards a constant. Since no finite size variational calculation is expected to give the exact binding energy, it is not surprising that the basis set is unable to give $\langle \hat{P} \rangle = 0$. It is clear that increasing $\lambda$ beyond a certain maximum value does not improve the degree of orthogonality with the core states. It will be seen later in the plots of the binding energies and annihilation rates versus $\lambda$ that the use of an excessively large $\lambda$ degrades the quality of the wave function as it attempts to satisfy a condition that is difficult to fulfill with a finite basis.

One of the noticeable features of Fig. 6 is the fact that $\langle \hat{P} \rangle$ is almost constant for the NaPs(600) and NaPs(870) wave functions when $10^2 < \lambda < 10^5$. Dividing the penalty function expectation by the energy (relative to the Na$^+$ core) gives $\langle \hat{P} \rangle/E \approx 1.5 \times 10^{-4}$ for the NaPs(870) basis. In a situation where the basis set is clearly limited in its ability to describe the true wave function it is probably not surprising that it is difficult to decrease the penalty function beyond a certain fraction of the total energy functional. The fact that the better quality NaPs(870) basis has lower values of $\langle \hat{P} \rangle$ is certainly consistent with this idea.

Another set of plots of the binding energies versus $\lambda$ are depicted in Fig. 7 to expose the fine details of the $\lambda$ dependence when $\lambda > \lambda_{\text{crit}}$. The Na$^-$ and Nae$^+$ curves are almost perfect step functions. There is of course some residual $\lambda$ dependence, but size of the variation (e.g. the Nae$^+$ binding energy changes from 0.00047300 to 0.00047262 Hartree when $\lambda$ changes from $10^5$ to $10^6$ Hartree) is sufficiently small to be of no practical importance. While the NaPs(600) and NaPs(870) binding energy curves resemble step functions, the $\lambda$ dependence is visible. The $\lambda$ dependence does not reveal a fundamental problem with the OPP Hamiltonian, rather it is a consequence of the finite basis sets being used. The larger NaPs(870) basis set shows less variation with $\lambda$ than the NaPs(600) basis set. It is noticeable that the NaPs(600) and NaPs(870) energies start to increase as $\lambda$ increases from $10^5$ Hartree. This increase is almost totally due to the $\hat{P}$ penalty function. When $\lambda$ increases from $2.0 \times 10^6$ to $1.0 \times 10^7$ Hartree, $\langle \hat{P} \rangle$ increases by $1.54 \times 10^{-2}$ Hartree while the energy increases by $1.60 \times 10^{-3}$ Hartree. The use of an excessively large value of $\lambda$ leads to a degradation of the computed binding energy.

The Nae$^+$ and NaPs systems will both decay by 2$\gamma$ annihilation since they contain a positron [15–17]. The dependence of the annihilation rate ($\Gamma$) with $\lambda$ is shown for both of these systems in Fig. 8. The computed annihilation rates shown in Fig. 8 only allow for the annihilation of the positron with the valence electron(s). The $\lambda$ dependence of $\Gamma$ is almost a perfect step function for Nae$^+$. The NaPs(600) and NaPs(870) annihilation rates curves are also very good approximations to a step function with the only visible $\lambda$ dependence for $\lambda > \lambda_{\text{crit}}$ occurring for $\lambda > 10^5$ Hartree. The decrease in $\Gamma$ at these very large values of $\lambda$ is a consequence of the decreasing wave function quality for excessively large $\lambda$ values.
With the atomic properties having a weak $\lambda$ dependence for $\lambda > \lambda_{\text{crit}}$, the obvious question would seem to be “at what value of $\lambda$ should final results be presented?” For some systems, this question is of minor importance since the energy and wave function show almost no variation with $\lambda$ as long as $\lambda > \lambda_{\text{crit}}$. However, there would seem to be two sensible choices of $\lambda$ for a system like NaPs for which an accurate solution of the Schrödinger equation is difficult to achieve. One viewpoint would assert that the aim should be to use the wave function that has the maximum degree of orthogonality with the core. This would suggest that choosing $\lambda = 10^5$ Hartree would be the best choice for the NaPs(870) wave function since a larger value of $\lambda$ would lead to a degradation in the wave function and not decrease the overlap with the core orbitals (this maximum sensible choice for $\lambda$ will obviously depend on the basis size and system under investigation). The NaPs(870) binding energy at $\lambda = 10^5$ Hartree was 0.008009 Hartree and the $2\gamma$ annihilation rate was $2.072 \times 10^9$ s$^{-1}$. Alternatively, $\lambda$ could be chosen to be some number just larger than $\lambda_{\text{crit}}$. The justification for this choice would be that the error inherent in using $(H + \lambda \hat{P})$ as an approximation to $QHQ$ is smaller than the error that results from the use of a finite basis set. The choice of $\lambda = 10^2$ Hartree would give a binding energy of 0.008449 Hartree and an annihilation rate $2.079 \times 10^9$ s$^{-1}$. Although these two values of $\lambda$ differ by 3 orders of magnitude, the derived binding energies differ by 5% and the annihilation rates differ by less than 1%.
We prefer to use a conservative estimate of the binding energy and therefore use the NaPs(870) wave function computed with $\lambda = 10^5$ Hartree. The energy and annihilation rate obtained from this wave function are the best so far achieved for the NaPs system and should be regarded as superseding values obtained in a previous calculation [17].

3. Discussion and conclusions

The OPP method of Kukulin of Krasnopolsky [9] has been examined for a model two level system and it has been shown the OPP procedure will produce energies that converge to those of the $\hat{Q}\hat{H}\hat{Q}$ Hamiltonian from below with a $O(1/\lambda)$ correction factor. Calculations for a number of complicated many body systems reveal that basis set effects can influence the ability of any calculation to produce wave functions with a zero overlap with the Pauli forbidden states just like they can influence the ability of a calculation to reproduce the exact eigenvalue. One significant feature of this work was the demonstration that the Pauli forbidden states are largely purged from the wave function once the OPP strength parameter $\lambda$ exceeds a certain critical value $\lambda_{crit}$, that is approximately equal to the single particle energy of the core level.

One subtle point that has not been mentioned in the previous discussion is the relationship between the model Hamiltonian and the wave function for the core orbitals. Our core orbitals were derived from a Hartree–Fock calculation while the model potential used the direct and exchange potentials calculated from the Hartree–Fock core orbitals (with some additional polarisation potentials). Therefore, the Pauli excluded states are quite close to being exact eigenstates of the unprojected Hamiltonian (i.e. $\beta$ is small) and this seems to be consistent with the very sharp drops in $\langle \hat{P} \rangle$ once $\lambda_{crit}$ is exceeded. The extent to which the Pauli forbidden components are excluded from the wave function could be adversely affected if the consistency between the core orbitals and underlying Hamiltonian was broken. For instance, one could use core orbitals taken from a Hartree–Fock potential but replace the Hartree–Fock core potential with a parametrised local potential [3]. In such circumstances the ability of $\langle \hat{H} + \lambda \hat{P} \rangle$ to faithfully reproduce the spectrum of $\hat{Q}\hat{H}\hat{Q}$ might be affected at values of $\lambda$ just larger than $\lambda_{crit}$.

The present numerical results can be used to place the related projection operator technique of Bonifacic and Huzinaga [3,10] into perspective. They use a functional form identical to Eq. (5) with the restriction that $\lambda$ is set to a particular value. To be specific, a different $\lambda$ is chosen for each projecting orbital and $\beta$ is set to be twice the absolute value of the Koopman energy. This choice was motivated by an analysis of the Lagrange multipliers and their operator equivalents that are used enforce to orthogonality amongst the different single particle solutions of the Hartree–Fock equations. This choice of Huzinaga and coworkers amounts to choosing $\lambda$ to be not much larger than $\lambda_{crit}$.

Another potential application of this procedure lies in the area of electron and positron atom scattering. The inclusion of the Pauli principal in electron–atom scattering calculations using the momentum space Lippmann–Schwinger equation is nontrivial [22]. At present there exists no general procedure for doing this and it is possible the OPP method may permit some progress to be made on this topic. Positronium formation is an integral part of the most sophisticated calculations of positron–atom scattering. There is a nonzero overlap between the electron in a Ps channel and the electrons in the rest of the atom. At present, this overlap is completely ignored in positron–atom calculations. The OPP is sufficiently simple that it may be possible to incorporate into calculations of positron–atom scattering.

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