Formal Analysis of Effective Core Potential Methods

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Effective core potentials are analyzed from the standpoint of the underlying frozen core approximation. The content of the pseudoorbital, the content of the potential, and the properties of both are elaborated, showing the points at which they differ from the frozen core approximation and where possible deficiencies might lie.

I. INTRODUCTION

Effective core potentials (ECPs) are in common use in quantum chemical calculations, in particular for heavy elements where relativistic effects can be incorporated into the potential. The foundation for the development of ECPs is the generalized Philips−Kleinman (GPK) pseudopotential (PP) method,[1,2] which was explored in some detail by Kahn et al.[3,4] These pseudopotentials depend on both the orbitals and the atomic state used to derive them, as are all pseudopotentials derived from the same underlying theory, but it is assumed that they are reasonably well transferable from atoms to molecules. The large number of calculations (see the review by Pyykkö and Stoll[5] for an analysis and for references to some 15 review articles) performed with PPs or ECPs attests to the general validity of this assumption.

In the early development of ECPs the Kahn procedure[3,4] for deriving pseudoorbitals (POs), which has a rigorous foundation in PP theory, was found to produce significant errors in molecular properties. This led to the development of the shape-consistent POs[6] which provided vastly improved results, which has been adopted as the standard procedure for generating POs and PPs. There have nonetheless been a number of more recent failures in the application of pseudopotential methods,[7,8] which has stimulated efforts toward understanding the reasons for the failures.[8−10] Titov and co-workers[11,12] trace some of them to the use of an outer-core pseudopotential for the valence orbitals of the same symmetry, and propose corrections to the PPs which are orbital specific. Some have also been due to the procedure used to define the pseudopotentials.[13]

In all of these examinations there is some analysis of the methodology but as yet no complete and rigorous analysis of PP theory as it is currently practiced. It is the aim of this paper to make such an analysis, and to assess from a formal standpoint the effects of the approximations made. These are to remove the core orbitals from explicit consideration, and replace their effect by a (preferably) one-particle potential, and to eliminate the core basis functions from the valence orbitals—a matter of efficiency for large molecular calculations, because the number of functions required to describe the inner part of the orbitals is usually large. In doing so, much of the work done previously must be reviewed and will be referenced where appropriate.

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Some disclaimers must be added at the outset. It is not the intention of this article to provide comparisons of numerical parameters or to assess the numerical accuracy of the sets of ECPs in the literature. This is an entirely different task which, for a proper assessment, would involve a great deal of computing with methods which have only recently become available.[14] It is also not the intention of this article to examine the ab initio model potentials[15] which are sometimes referred to as ECPs—worthy as this task may be. These, although they also rely on the frozen core approximation, retain explicitly the core orbitals in a projector and also the core parts of the valence orbitals. Here the focus is on the PPs as defined in the previous paragraph, with no explicit core orbitals or core basis functions.

II. THE FROZEN CORE APPROXIMATION

The starting point for the development of ECPs is the frozen core approximation. For the purposes of the analysis of this paper, we work within the framework of a complete set of orthonormal orbitals. These orbitals satisfy some kind of one-particle Schrödinger equation, which means that they must be finite, continuous, and differentiable to all orders, except at the nuclear cusp. The n_c core orbitals selected from this set are fully occupied in all possible configurations. The wave function is partitioned into a core and a valence part

$$\Psi(1,...,N) = \hat{A}\,\Psi_c\,(1,...,2n_c)\,\Psi_v(2n_c+1,...,N) \quad (1)$$

where the core wave function is

$$\Psi_c(1,...,2n_c) = \hat{A}\prod_i^{n_c}\phi_{i\alpha}\phi_{i\beta} \quad (2)$$

We now omit the explicit consideration of the core orbitals in the wave function and work with valence wave functions. The valence Hamiltonian for any valence state with this frozen core may be written (with the core energy removed) as

$$\hat{H}_v = \sum_i F^c(i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} \quad (3)$$

where the core Fock operator is

$$F^c(i) = \hat{h}_i + 2\hat{J}^c(i) - \hat{K}^c(i) \qquad (4)$$

and $\hat{J}_c$ and $\hat{K}_c$ are the usual core Coulomb and exchange operators

$$\hat{J}_c(i) = \sum_c \int d^3 r_j \frac{\phi_c(j)^* \phi_c(j)}{r_{ij}},$$

$$\hat{K}^c(i) \phi(i) = \sum_c \int d^3 r_j \frac{\phi_c(j)^* \phi(j)}{r_{ij}} \phi_c(i) \quad (5)$$

If the valence orbitals remain orthogonal to the core and are not approximated in any way, no further changes to the Hamiltonian are needed. This is in fact the Hamiltonian used in most configuration interaction calculations.

In molecular calculations, it is usually not convenient or efficient to work within a basis set constructed from a set of orbitals which are orthogonal to the core orbitals of a particular atom, because the orthogonalization procedure introduces into the calculation components of the core, and the integrals must be evaluated over all the core basis functions. It is therefore expedient to define a pseudoorbital in which the core components have been removed. From the properties of determinants, we may always introduce a linear combination of the core orbitals into the valence orbitals without affecting the total energy:

$$\chi_v = \phi_v + \sum_c^{n_c} a_{cv} \phi_c = \phi_v + \phi_v^R \qquad (6)$$

The core part ϕ_v^R will be termed the residual orbital or the core tail. Note that at this stage we do not renormalize the pseudoorbital χ_v.

In order to make use of pseudoorbitals, we need to insert projection operators onto the valence space into the Hamiltonian. Defining the core and valence projection operators

$$\hat{P}^c = \sum_c^{n_c} |\phi_c\rangle\langle\phi_c|, \quad \hat{P}^v = 1 - \hat{P}^c \qquad (7)$$

it is easy to show that

$$(1 - \hat{P}^c)\chi_v = \hat{P}^v \chi_v = \phi_v \qquad (8)$$

All operators in principle now become *N*-particle operators: for example

$$\hat{h}(i) \to \hat{P}^v(i) \hat{h}(i) \hat{P}^v(i) \prod_{j \neq i} \hat{P}^v(j) \qquad (9)$$

However, if a modified metric is defined

$$\hat{G}(i) = \hat{P}^v(i) \qquad (10)$$

for which

$$\langle\chi_v|\hat{G}|\chi_{v'}\rangle = \delta_{vv'} \qquad (11)$$

it is not necessary to explicitly consider the change in metric in all the operators. The valence Hamiltonian operator now becomes

$$\hat{H}_v = \sum_i \hat{P}^v(i) F^c(i) \hat{P}^v(i) + \frac{1}{2}\sum_{i \neq j} \hat{P}^v(i) \hat{P}^v(j) \frac{1}{r_{ij}} \hat{P}^v(j) \hat{P}^v(i) \qquad (12)$$

which may be partitioned into an unmodified operator plus a pseudopotential

$$\hat{H}_v = \sum_i \hat{h}(i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}} + V^{FCPP} \qquad (13)$$

The content of V^{FCPP} is found by subtraction from (12) with susbstitution of $\hat{P}^v$ from (7)

$$V^{FCPP} = \sum_i 2J^c(i) - K^c(i) + [-\hat{P}^c(i) F^c(i) - F^c(i) \hat{P}^c(i) +$$

$$\hat{P}^c(i) F^c(i) \hat{P}^c(i)] + \frac{1}{2} \sum_{i \neq j} [-\hat{P}^c(i) - \hat{P}^c(j) + \hat{P}^c(i) \hat{P}^c(j)]$$

$$\frac{1}{r_{ij}} + \frac{1}{r_{ij}} [-\hat{P}^c(i) - \hat{P}^c(j) + \hat{P}^c(i) \hat{P}^c(j)] + [-\hat{P}^c(i) - \hat{P}^c(j)$$

$$+ \hat{P}^c(i) \hat{P}^c(j)] \frac{1}{r_{ij}} [-\hat{P}^c(i) - \hat{P}^c(j) + \hat{P}^c(i) \hat{P}^c(j)] \quad (14)$$

This complicated operator contains both one- and two-electron terms. The only dependence it has on the electronic structure of the species under consideration is the definition of the core.

It may be noted in passing that the direct use of this approach with an approximation to the core projectors was developed by Leasure et al.[16]

III. THE GENERALIZED PHILIPS−KLEINMAN PSEUDOPOTENTIAL

The current generation of pseudopotentials involves further approximations to the frozen core pseudopotential operator and the corresponding metric. In particular, they seek to remove *all* explicit reference to core orbitals. The theoretical foundation rests on the generalized Philips−Kleinman (PK) approach,[1,2] and is presented here with an analysis of the consequences of the extension of the method to many-electron atoms.

The generalized PK PPs are derived from the all-electron Hartree−Fock (HF) equation for a given atomic orbital. The discussion will be restricted to closed-shell atoms for simplicity, because open-shell atoms do not add any new features of principle. The HF equation can be written

$$\hat{F}\phi_i = \sum_j^{occ} \epsilon_{ji}\phi_j \qquad (15)$$

where $\hat{F}$ is the Fock operator

$$\hat{F} = \hat{h} + \sum_j^{occ} 2\hat{J}_j - \hat{K}_j \qquad (16)$$

and the ϵ_{ji} are the Lagrange multipliers introduced to ensure orbital orthogonality; they are defined by

$$\langle j|\hat{F}|i\rangle = F_{ji} = \epsilon_{ji} \qquad (17)$$

For a valence orbital ϕ_i it is always possible to insert the

valence projection operator into (15), and then

$$(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)\phi_i = \sum_j^{occ} \epsilon_{ji}(1 - \hat{P}^c)\phi_j \quad (18)$$

This equation is now satisfied by the pseudoorbitals χ_i and χ_j as well, which may replace ϕ_i and ϕ_j in the above equation. It is also worth noting that this is precisely the equation we would get from the projected frozen core Hamiltonian.

The next step is to combine all terms involving the core projectors into a PP. For a single orbital outside the core the only term surviving on the right-hand side involves the valence PO. We may then transfer the core projector to the left-hand side to obtain the equation

$$\hat{F} + \hat{V}_i^{GPK} \chi_i = \epsilon_i \chi_i \quad (19)$$

where the generalized Philips−Kleinman (GPK) pseudo-potential is

$$\hat{V}_i^{GPK} = -\hat{P}^c \hat{F} - \hat{F}\hat{P}^c + \hat{P}^c \hat{F} \hat{P}^c + \epsilon_i \hat{P}^c \quad (20)$$

Since the core orbitals are eigenfunctions of $\hat{F}$, the GPK PP can be written

$$\hat{V}_i^{GPK} = \sum_c (\epsilon_i - \epsilon_c)|\phi_c\rangle\langle\phi_c| \quad (21)$$

The transfer of the core projector into the potential has some important consequences. First, it makes the PP orbital-specific because the transfer includes the orbital eigenvalue. Second, because it replaces the frozen core metric operator $(1 - \hat{P}^c)$ by unity, the PO, which was normalized on the frozen core metric operator, is no longer normalized.

Extending the GPK method to more than one valence orbital of a given symmetry, the HF equations for two orbitals ϕ_i and ϕ_j from a closed-shell atom are

$$(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)\phi_i = \epsilon_i(1 - \hat{P}^c)\phi_i + \epsilon_{ji}(1 - \hat{P}^c)\phi_j \quad (22)$$

$$(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)\phi_j = \epsilon_j(1 - \hat{P}^c)\phi_j + \epsilon_{ij}(1 - \hat{P}^c)\phi_i \quad (23)$$

As before, we may substitute the pseudoorbitals for the HF orbitals. We wish to transfer the core projector terms into the PP, but now there is a problem. The diagonal term may be transferred as before, but what of the off-diagonal Lagrange multiplier term?

There are two ways we could approach this problem. The first is that we may set them to zero since we are using canonical Hartree−Fock orbitals. Then we only have the diagonal terms, and we end up with

$$[(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c) + \epsilon_i\hat{P}^c]\chi_i = \epsilon_i \chi_i \quad (24)$$

$$[(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c) + \epsilon_j\hat{P}^c]\chi_j = \epsilon_j \chi_j \quad (25)$$

Now we have two separate PPs, one for each PO, but unlike the open-shell HF equations where there are different Fock operators for orbitals with different occupations, here there are different pseudo-Fock operators for POs with the same occupation. The canonical HF orbitals had the same Fock operator; now the POs have different Fock operators.

The second way is to define the Lagrange multipliers in terms of the pseudoorbitals as

$$\epsilon_{ji} = \langle\chi_j|(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)|\chi_i\rangle \quad (26)$$

and substitute for both the diagonal and off-diagonal terms. Transferring the core projector terms to the PP, we have

$$[(1 + \hat{P}^c\hat{P}^{\bar{v}})(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)]\chi_i = \epsilon_i\chi_i + \epsilon_{ji}\chi_j \quad (27)$$

$$[(1 + \hat{P}^c\hat{P}^{\bar{v}})(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c)]\chi_j = \epsilon_j\chi_j + \epsilon_{ij}\chi_i \quad (28)$$

where the overline indicates the use of the POs in the operator, i.e.

$$\hat{P}^{\bar{v}} = \sum_i |\chi_i\rangle\langle\chi_i| \quad (29)$$

We now have only one PP, which is dependent on both orbitals i and j—or, in general, on all the valence POs. However, the POs are not eigenfunctions of this PP. Writing the pseudo-Fock operator as

$$\hat{F}^{PP} = (1 + \hat{P}^c\hat{P}^{\bar{v}})(1 - \hat{P}^c)\hat{F}(1 - \hat{P}^c) \quad (30)$$

we find that the matrix elements over the valence POs can be written as a product of the orbital eigenvalue and the overlap. The matrix eigenvalue equation in the valence space is then

$$\mathbf{F}^{PP}\mathbf{C} = \epsilon\mathbf{S}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \quad (31)$$

where ϵ is the diagonal matrix of HF orbital eigenvalues and E is the diagonal matrix of eigenvalues of the PP Fock operator $\mathbf{F}^{PP}$. Clearly we may make the substitution $\mathbf{X} = \mathbf{SC}$, and we find that the eigenvalues are the HF eigenvalues ϵ, and the eigenvectors can be shown to be $\mathbf{C} = \mathbf{S}^{-1}$. What this means is that the POs are *not* eigenfunctions of this PP, but linear combinations of them are, with the same eigenvalues. It also means that since $\mathbf{C}$ is not unitary, the eigenfunctions are not rotations of the canonical orbitals, and hence the PP valence energy is different from the true valence energy. One further disadvantage of this PP is that it is not Hermitian.

Whichever approach we choose, the transfer of the core projector terms to the PP changes the metric, and this change in metric has consequences for orbital orthogonality. The POs were orthogonal on the frozen core metric, so they cannot in general also be orthogonal on the unit metric. The overlap of two POs on the unit metric is

$$\langle\chi_i|\chi_j\rangle = \sum_c a_{ci}a_{cj} = \langle\phi_i^R|\phi_j^R\rangle \quad (32)$$

i.e., the overlap is the overlap of the core tails, which cannot in general be zero. One need only consider the case of a single core orbital, where a_{ci} must be nonzero, to see that this is the case. Since the coefficients of the core orbitals are determined already, to minimize the core part of the PO, making the POs orthogonal amounts to an extra condition on the coefficients which would degrade the minimization. Moreover, the core tails of valence HF orbitals are very similar, so that the imposition of the condition of orthogonality of the core tails would force one of the POs to have a large core contribution. This would defeat the purpose of

EFFECTIVE CORE POTENTIAL METHODS

J. Chem. Inf. Comput. Sci., Vol. 41, No. 1, 2001 **33**

the construction of POs, which is to eliminate the core part of the valence orbitals.

The similarity of the core tails of the valence orbitals can be demonstrated by an experiment with a generally contracted basis set, in which basis functions are successively removed from the contracted set, starting from the outermost. The overlap of the contracted functions after the removal of each basis function is monitored for linear dependence. Consider the Hg atom, for example. We remove the functions used to describe the outermost maximum of the 6s orbital for valence flexibility, as usual. Then when the functions used to describe the outermost maximum of the 5s orbital are removed, the residue of the 6s orbital becomes linearly dependent on the residue of the 5s orbital and the other core orbitals. We infer from this that the coefficients of the core tails are linearly dependent, i.e.

$$a_{ci} = \lambda a_{cj}, \quad c = 1, ..., i - 1 \tag{33}$$

If this is so, it would make it impossible to construct orthogonal POs since the core tail overlap could not be made zero.

Since the transfer of the core projector into the metric in the first approach to the generalization of the PK PP makes the PPs orbital specific and the POs nonorthogonal, one is then faced with the prospect of generating a PP for each PO required—occupied and virtual—and including projectors onto each PO. Titov and co-workers[11,12] proceed at least partway down this route. The alternative of creating a non-Hermitian PP is equally undesirable. The procedure that is adopted in most formulations of ECPs is to generate the PP for the lowest PO and make use of the higher eigenfunctions of this PP to approximate the higher POs.

To analyze the effect of this approximation, we expand the solutions in terms of the nonorthogonal POs, giving a generalized eigenproblem with Fock matrix

$$F_{kj} = \langle \chi_k | (1 - \hat{P}^c) F (1 - \hat{P}^c) + \epsilon_i \hat{P}^c | \chi_j \rangle = \epsilon_j \delta_{kj} + \epsilon_i S_{kj}^{\mathrm{R}} \tag{34}$$

and metric

$$S_{kj} = \langle \chi_i | \chi_j \rangle = \delta_{kj} + S_{kj}^{\mathrm{R}} \tag{35}$$

where

$$S_{kj}^{\mathrm{R}} = \langle \phi_k^{\mathrm{R}} | \phi_j^{\mathrm{R}} \rangle \tag{36}$$

is the overlap between the core tails. This system of equations has χ_i as the lowest eigenfunction with eigenvalue ϵ_i, as expected. By subtracting ϵ_i from the eigenvalue, the Fock matrix becomes diagonal

$$F'_{kj} = \epsilon_j \delta_{kj} \tag{37}$$

but the metric remains the same. The fact that the metric is nondiagonal means that the higher eigenfunctions must mix in some of the lowest PO to maintain orthogonality. Since the trace of the metric is greater than 1, the eigenvalue spectrum is compressed compared to the HF spectrum, and this means that the use of ECPs for excited states is likely to give excitation energies which are too low.

Some evidence for this may be seen in the experiments of Lee et al.[17] on the Au atom, where they observed that the

6s eigenvalue comes closer to the 5s eigenvalue when the s PP is determined for the 5s orbital. This was attributed to the difference in exchange energies since the two orbitals have different Fock operators. However, the valence 6s orbital is now being determined in the potential of the core Fock operator, and the difference in the diagonal element is

$$\langle \chi_v | F^c | \chi_v \rangle - \langle \chi_v | F^v | \chi_v \rangle = \left\langle \chi_v \left| J_v - \frac{1}{2} K_v \right| \chi_v \right\rangle = \frac{1}{2}(vv|vv) \tag{38}$$

which is positive. The eigenvalue ought therefore to move in the opposite direction from that observed, i.e., further away from the 5s rather than closer. The effect on the eigenvalue is therefore due to the compression of the spectrum, not the difference in Fock operator. The compression of the spectrum is also seen in the excitation energies for Xe and Xe⁺ from the same work.

We now turn to the specific form of the PP itself. At this stage we must consider the normalization of the POs, which has been neglected until now. The norm of the PO must be greater than unity because of the addition of the core tail part, and the normalized PO is

$$\tilde{\chi}_v = \frac{1}{\sqrt{1 + S_{vv}^{\mathrm{R}}}} (\phi_v + \phi_{\ v}^{\mathrm{R}}) \tag{39}$$

The renormalization will affect the wave function because we are scaling one of the rows in the determinant. It does not of itself affect the energy because the scaling factor cancels.

The PP derived from the HF equation is defined by

$$\hat{h}' + 2\tilde{J}^{\mathrm{val}} - \tilde{K}^{\mathrm{val}} + \hat{V}^{\mathrm{PP}} = \hat{F} + \hat{V}^{\mathrm{GPK}} \tag{40}$$

The one-electron operator is modified to include in the PP the portion of the nuclear attraction which balances the Coulomb repulsion of the core electrons. The tilde on the operators indicates that the normalized POs are to be used in constructing the operator. Clearly the whole of $\hat{V}^{\mathrm{GPK}}$ is included in the PP. The Fock operator may be partitioned into a core and a valence part

$$\hat{F} = \hat{T} - \frac{Z_c}{r} + \sum_c (2\hat{J}_c - \hat{K}_c) - \frac{Z_v}{r} + \sum_v (2\hat{J}_v - \hat{K}_v) \tag{41}$$

and we may substitute for the POs in the valence two-electron terms to obtain

$$2\tilde{J}^{\mathrm{val}} - \tilde{K}^{\mathrm{val}} = \sum_v \frac{1}{1 + S_{vv}^{\mathrm{R}}} (2\hat{J}_v - \hat{K}_v + 2\hat{J}_v^{\mathrm{R}} - \hat{K}_v^{\mathrm{R}}) \tag{42}$$

where the residual Coulomb potential can be written in terms of the core tails as

$$\hat{J}^{\mathrm{R}}{}_v(i) = \int \mathrm{d}^3 r_j \frac{\phi_v^{\mathrm{R}}(j)^* \phi_v(j) + \phi_v(j)^* \phi_v^{\mathrm{R}}(j)}{r_{ij}} +$$
$$\int \mathrm{d}^3 r_j \frac{\phi_v^{\mathrm{R}}(j)^* \phi_v^{\mathrm{R}}(j)}{r_{ij}} \tag{43}$$

The exchange term can be similarly expressed. With this

information, the PP may now be expressed as

$$\hat{V}^{PP} = -\frac{Z_c}{r} + \sum_c (2\hat{J}_c - \hat{K}_c) + \hat{V}^{GPK} +$$
$$\sum_v \frac{1}{1 + S_{vv}^R}(S_{vv}^R(2\hat{J}_v - \hat{K}_v) - (2\hat{J}_v^R - \hat{K}_v^R)) \quad (44)$$

As well as the expected core terms, there is a core tail term in the PP and a scaled valence term.

The renormalization of the PO was found in early developments of PPs to be the cause of significant problems.[4,6] Christiansen et al.[6] observed that, outside the radius of the core, the renormalization of the PO means that the valence electron density has been reduced, and the missing density appears in the core. The consequence of this is that there is less Coulomb repulsion in the valence region, and the PP has an attractive long-range tail in the valence region. This is canceled out when the potential due to the valence POs is added, so the Fock operator is the same whether or not the POs or the canonical HF orbitals are used to construct it. This is a feature of PK PPs: the Fock operator is invariant to the choice of POs.

The cancellation of the long-range attraction in the PP by the valence two-electron PO terms is complete only for the state of the atom in which the PO and PP were derived. In molecules, the valence density is in general reduced from the atomic value, so the cancellation will leave a small net attraction in the valence region. The influence of this on molecular properties would be a decrease in bond length and increase in dissociation energy, both of which were observed in early PP calculations. The molecular potential will be sensitive to the cancellation, creating possible instability problems in the calculations and certainly giving erroneous results. This problem led to the development of the *shape-consistent* POs and the corresponding PPs, which will be considered in the next section.

IV. SHAPE-CONSISTENT PSEUDOORBITALS

The proposal made by Christiansen et al. to overcome the problem of renormalization of the valence portion of the PK POs was to replace the core part of the HF orbitals with a smooth polynomial function up to some matching point. The function is chosen to have the minimum number of turning points and to preserve the norm; the coefficients are determined by equating the derivatives of the polynomial and the HF orbital at the matching point. The resulting POs are called shape-consistent POs (SCPOs) because they preserve the shape of the HF orbital in the valence region (and more importantly the amplitude).

This procedure introduces some interesting features in the formal analysis. What is added to the HF orbital is a function which is confined to the core region and hence is obviously square integrable. The norm of the SCPO is still unity. We write the SCPO as

$$\chi_v(r) = \phi_v(r), \quad r > R_c$$
$$= p_v(r), \quad r < R_c \quad (45)$$

and define the core tail as

$$f_v(r) = \chi_v(r) - \phi_v(r) \quad (46)$$

f_v is obviously confined to $r < R_c$. From the normalization requirement we deduce that

$$2\langle\phi_v|f_v\rangle + \langle f_v|f_v\rangle = 0 \quad (47)$$

implying that the overlap between the HF orbital and the core tail must be negative. For the SCPO to be a valid orbital, it must be able to be expanded in the complete orthonormal set of orbitals of which the HF orbital is a member. If we make the expansion

$$f_v = \sum_i a_{vi}\phi_i \quad (48)$$

and substitute into eq 47, we find that

$$2a_{vv} + \sum_i a_{vi}{}^2 = 0 \quad (49)$$

In order for the core tail to be nonzero, we must have $a_{vv} <$ 0, i.e., the "core tail" of the SCPO must contain a contribution from the valence orbital, and this contribution must be negative, so that the weight of the valence HF orbital in the SCPO is less than one.

The presence of the valence orbital in the core tail also means that the core tail must contain contributions from other orbitals which have a significant amplitude in the valence region to cancel the valence orbital for $r > R_c$, and these must be noncore orbitals. We are therefore mixing virtual orbitals into the valence SCPO. Essentially what we have done is an expansion of the SCPO in the complete orthonormal set with renormalization. The coefficients are chosen so that the core part becomes smooth and the valence part reproduces the valence orbital amplitude.

The introduction of virtual orbitals in the SCPO changes the valence wave function and energy, which the PKPO does not do. For illustration, consider the case of two electrons outside a core with

$$\chi_v = (\phi_v + b\phi_a)\big/\sqrt{1 + b^2} \quad (50)$$

for which the valence wave function is

$$|\chi_{v\alpha}\chi_{v\beta}| = \frac{1}{1 + b^2}|\phi_{v\alpha}\phi_{v\beta}| + \frac{b^2}{1 + b^2}|\phi_{a\alpha}\phi_{a\beta}| +$$
$$\frac{b}{1 + b^2}|\phi_{v\alpha}\phi_{a\beta} - \phi_{v\beta}\phi_{a\alpha}| \quad (51)$$

The last term is a Brillouin single excitation from the original valence wave function. In this example we have no core orbitals in the PO, and hence we can use the frozen core Hamiltonian to evaluate the energy. The new valence energy is

$$E' = E^{val} + \frac{2b^2}{(1 + b^2)}(\epsilon_a - \epsilon_v + 3K_{va} - J_{va}) +$$
$$\frac{b^4}{(1 + b^2)^2}(J_{vv} + J_{aa} - 2J_{va} - 4K_{va}) \quad (52)$$

The largest contribution comes from the second term. For

EFFECTIVE CORE POTENTIAL METHODS

J. Chem. Inf. Comput. Sci., Vol. 41, No. 1, 2001 **35**

high-lying orbitals K_{va} and J_{va} will be small, but $\epsilon_a - \epsilon_v$ will not be small; for low-lying orbitals the opposite is the case.

In order to preserve the valence energy, therefore, it is necessary to freeze and project out the virtual orbitals as well as the core. However, due to the requirement that these be chosen to cancel the valence part of the core tail, they will not necessarily be the high-lying virtuals and may in fact be precisely the functions chosen for valence flexibility in molecular calculations. The alternative is to freeze out the particular linear combination which cancels the valence part of the core tail. In any case, we have an additional freezing of orbitals above the freezing of the core. The projection operator required is now

$$\hat{P}^v = 1 - \hat{P}^c - \hat{P}^a \qquad (53)$$

where

$$\hat{P}^a = \sum_a^{n_a} |\phi_a\rangle\langle\phi_a| \qquad (54)$$

It is clear that this projection operator functions in precisely the same way as the previous operator: applying it to the PO returns the valence HF orbital, with the same eigenvalue.

More than this, it is clear that precisely the same analysis can be applied to the SCPOs and the corresponding PPs as was applied to the PK POs and PPs, with the same conclusions. Regardless of the particular definition of the PO, it is the transfer of the core projector term from the metric to the PP which causes the problems: the POs are nonorthogonal, the PPs are either orbital specific or general but non-Hermitian, and using the lowest PP for all POs within a given symmetry will result in a compression of the virtual spectrum. However, the problem of the sensitivity to the valence occupation which existed in the GPK PPs has now been removed.

Before leaving the definition of the SCPO, one further point must be made. The polynomial function used to represent the core tail introduces discontinuities into the derivatives of the SCPO of higher order than the polynomial. As a result, the SCPO cannot strictly be represented in terms of the complete orthonormal set. The effect of this approximation is likely to be small, however, and the approximation normally employed of expansion in a Gaussian basis set which effectively removes the discontinuity is probably larger.

V. THE EFFECTIVE CORE POTENTIAL HAMILTONIAN

So far we have considered only the PO and the PP. We must now insert the PP into the Hamiltonian and study the effect of its insertion. The desired form of the Hamiltonian is one in which only the one-electron operator is modified

$$\hat{H}^v = \sum_i [\hat{h}'(i) + \hat{V}^{PP}(i)] + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} \qquad (55)$$

The sums run over valence electrons only.

For a closed-shell system, the valence energy can be written

$$E^{val} = \sum_i 2\langle i|\hat{F}^c|i\rangle + \sum_{ij}(2J_{ij} - K_{ij}) \qquad (56)$$

$$E^{val} = \sum_i 2\epsilon_i - \sum_{ij}(2J_{ij} - K_{ij}) \qquad (57)$$

where, in Mulliken notation, the Coulomb and exchange integrals are

$$J_{ij} = (ii|jj), \quad K_{ij} = (ij|ji) \qquad (58)$$

The same expressions may be used with POs and PPs by replacing $\hat{F}^c$ with $\hat{h}' + \hat{V}^{PP}$. Since the orbital eigenvalues are the same whether the PP is used or not—provided that we only include one PO in each symmetry in the valence space—the difference between the FC valence energy and the PP valence energy may be expressed in terms of the two-electron integrals. For the case of one orbital with two electrons in the valence space, for example, this reduces to

$$\Delta E^{val} = (\phi_v\phi_v|\phi_v\phi_v) - (\chi_v\chi_v|\chi_v\chi_v) \qquad (59)$$

Naturally, all that is required of the PP is that the valence energies themselves be equal. This is a requirement on only one quantity. However, for the PP to be useful in calculations other than the atomic calculation in which it was derived, it would be desirable for the Coulomb and exchange integrals themselves to be equal, and for correlated calculations, all the valence integrals should be equal. This would place too severe a constraint on the PP and the POs if these conditions were imposed to determine the POs.

Once the object of defining a PP Hamiltonian with no explicit reference to core orbitals has been achieved, it is important to ensure that if core orbitals were to appear in a calculation, they would not cause problems. Orbitals on neighboring atoms in a molecular calculation are a possible source of components of core orbitals, for example. We next examine the question of the stability of the HF equations derived from this Hamiltonian with respect to contamination of the PO by core orbitals. This is an issue because even though the PP was derived from the FC HF equations, the PP Hamiltonian is now different from the FC Hamiltonian.

To address this question, we consider the case of two electrons in a single orbital outside the core, giving a single PO. This is mixed with a core orbital and the energy expression as a function of the coefficient of the core orbital is examined to see if a zero coefficient is a minimum or not. We write the mixed PO as

$$\chi'_v = (\chi_v + \lambda\phi_c)\big/\sqrt{1 + 2\lambda S + \lambda^2} \qquad (60)$$

where χ_v is normalized. Making use of the definition of the PP, we can write the energy expression as

$$E = 2\epsilon_v + (v'v'|v'v') - 2(vv|v'v') + (vv'|v'v) \qquad (61)$$

and expanding out in terms of λ we find that

$$E = 2\epsilon_\nu + (vv|vv) -$$
$$\frac{\lambda^2}{(1 + 2\lambda S + \lambda^2)^2}[(\lambda + 2S)^2(vv|vv) + 4(\lambda + 2S)(cv|vv) +$$
$$(1 + 4\lambda S + 2\lambda^2)(cc|vv) - 2(3 + 2\lambda S + \lambda^2)(cv|vc) -$$
$$4\lambda(cc|cv) - \lambda^2(cc|cc)] \quad (62)$$

which is the energy for the unperturbed PO with a correction which is at least quadratic in λ. The point $\lambda = 0$ is clearly a stationary point, but the curvature is negative, not positive, which may be seen from the Hessian at the stationary point

$$\left.\frac{\partial^2 E}{\partial \lambda^2}\right|_{\lambda=0} = -2[(cc|vv) - 3(cv|vc) + 4S(cv|vv) +$$
$$2S^2(vv|vv)] \quad (63)$$

The dominant contribution is from $(cc|vv) >> (cv|vc)$. The conclusion is that there will be a tendency for the PO to mix in some core orbital character in an optimization with the PP Hamiltonian. This makes it imperative that the representation of the core orbitals in the basis set be kept to a minimum.

VI. THE SEMILOCAL REPRESENTATION

The final stage in the development of effective core potentials is the representation in terms of operators which are implemented in computer codes. The standard practice is to make a semilocal representation which extends in angular momentum up to that of the highest occupied orbital in the core, and to extract out a common local term

$$\hat{V}^{ECP} = U^{local} + \sum_l^{l_{max}}[U_l - U^{local}]\sum_m |lm\rangle\langle lm| \quad (64)$$

where l_{max} is the maximum angular momentum of the core orbitals. The use of the semilocal approximation removes the necesssity for projection onto specific orbitals, and permits the selection of the PP of the appropriate angular symmetry. This embodies the use of the PP of the lowest valence orbital in each symmetry for all orbitals of the same symmetry. There are two approximations involved in this step: the truncation of the angular expansion and the semilocal approximation itself.

To analyze this approximation, we make use of eq 44. The PP can be divided into three parts: the local part, which includes the core part of the nuclear charge and the Coulomb contributions from the core and the core tails, the corresponding exchange terms which are nonlocal, and the core projector terms. The local part obviously contributes to U^{local} and need not be discussed. The core projector terms coming from the GPK PP clearly contribute to $U_l - U^{local}$, and only make contributions for $l \leq l_{max}$. The only approximation here is the semilocal approximation, which is valid by construction for the orbital for which the PP was generated.

It is the exchange terms that require some analysis. These can be written in terms of a projection onto a complete set of states, summed over radial and angular quantum numbers

$$\hat{K} \rightarrow \sum_{nlm} \sum_{n'l'm'} |nlm\rangle\langle nlm|\hat{K}|n'l'm'\rangle\langle n'l'm'| \quad (65)$$

The core exchange terms come from a closed shell, and for this special case the angular integrations provide the restrictions $l = l'$ and $m = m'$, reducing the representation of the exchange term to

$$\hat{K} \rightarrow \sum_{nn'} \sum_{lm} |nlm\rangle\langle nlm|\hat{K}|n'lm\rangle\langle n'lm| \quad (66)$$

and the semilocal approximation is justified on the same grounds as for the GPK PP. If the atomic state for which the PP is generated is not a closed-shell state, the restrictions do not apply. For example, if there is a single p orbital in the valence space, exchange terms in which $l = 0$ and $l' = 2$ are nonzero. It is then necessary to perform an average over all the valence states generated from the atomic configuration to obtain the same reduction of the sums.

The second aspect of the reduction of the exchange potential is the truncation of the sum. This depends on the contribution from the exchange potential being the same for all angular momenta higher than the cutoff, l_{max}. Using the simple approximation of a hydrogenic function with exponent α for the lowest orbital of each angular momentum, with the core represented by a 1s function with exponent γ, we arrive at

$$\frac{1}{(2\gamma)^3}\frac{\hat{K}\phi_{\alpha l}}{\phi_{\alpha l}} = \frac{(2l+2)!}{(\alpha+\gamma)^{2l+3}}\frac{e^{-(\gamma-\alpha)r}}{r^{2l+1}} - e^{-2\gamma r} \times$$
$$\left[\sum_{m=0}^{2l}\frac{(2l+2)!}{(2l-m)!}\frac{1}{(\alpha+\gamma)^{m+3}r^{m+1}} + \frac{(2l+1)}{(\alpha+\gamma)^2}\right] \quad (67)$$

None of the terms in this expression is independent of the angular momentum l, even if one were to choose the same exponent α for each l. However, the presence of high inverse powers of r suggests that the only important term is the last one, for which the only dependence on l is in the factor of $2l + 1$. This term must increase as l increases. The true picture will be more complicated, and experiments by Kahn et al.[3] indicate that the dependence on l for $l > l_{max}$ is not large. This may be simply due to the fact that as l increases, the orbitals do not penetrate the core as much and the magnitude of the exchange becomes small enough that the differences are negligible. However, it should be borne in mind that there may be significant effects for l values not much larger than l_{max} where the penetration of the higher angular momentum orbitals into the core is still significant. Such effects have been observed for large core PPs.[8,9]

The final step in representing the PPs is to perform a fit to some appropriate functional form. The most common of these is a combination of Gaussian functions with some powers of r.

DISCUSSION

It is clear that the development of PPs involves a number of approximations beyond the FC approximation. As mentioned in the Introduction, the success of PPs in molecular calculations attests to the general care taken in minimizing the effects of these approximations, and the general insensitivity of the calculated properties to the particular form of the PP. Since the development of the shape-consistent POs and the corresponding PPs, probably the most important areas

EFFECTIVE CORE POTENTIAL METHODS

J. Chem. Inf. Comput. Sci., Vol. 41, No. 1, 2001 **37**

where deficiencies in the PPs might lie are in the use of a single PP for each angular symmetry with the consequent compression of the spectrum, and the truncation of the angular expansion in the exchange. The latter is fairly readily addressed by deriving PPs for higher angular momenta than exist in the core.

The compression of the spectrum presents a dilemma, especially for the heavy elements. If only one occupied orbital of each symmetry is represented, the core may be too large to freeze for accurate calcuations; if more orbitals are included in the core, the valence orbitals may be too low in energy. To remain within the semilocal form of the PP, the approach that probably goes the furthest in resolving this problem is that of the Stuttgart group. Here the PP is adjusted to minimize the error in a range of energetic properties, computed at the all-electron and PP levels. This is equivalent to performing some sort of averaging of the individual PPs and adjustment of the POs to obtain the best fit to a larger parameter set. These PPs are termed *energy-adjusted* PPs. In this way the states which are important for the bonding of the atom are well-described. Moreover, it is possible within this scheme to provide a good description of states which are quite different from the ground state of the atom.

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REFERENCES AND NOTES

(1) Phillips, J. C.; Kleinman, L. *Phys. Rev.* **1959**, *116*, 287.
(2) Weeks, J. D.; Rice, S. A. *J. Chem. Phys.* **1968**, *49*, 2741.
(3) Kahn, L.; Baybutt, P.; Truhlar, D. G. *J. Chem. Phys.* **1976**, *65*, 3826.
(4) Hay, P. J.; Wadt, W. R.; Kahn, L. R. *J. Chem. Phys.* **1978**, *68*, 3059.
(5) Pyykkö, P.; Stoll, H. Royal Society of Chemistry, Specialist Periodical Reports, Chemical Modelling, Applications and Theory, 2000.
(6) Christiansen, P. A.; Lee, Y. S.; Pitzer, K. S. *J. Chem. Phys.* **1979**, *71*, 4445.
(7) Dyall, K. G. *J. Chem. Phys.* **1992**, *96*, 1210.
(8) Schwerdtfeger, P.; Fischer, T.; Dolg, M.; Igel-Mann, G.; Nicklass, A.; Stoll, H.; Haaland, A. *J. Chem. Phys.* **1995**, *102*, 2050.
(9) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1996**, *105*, 1052.
(10) Dolg, M. *J. Chem. Phys.* **1996**, *104*, 4061.
(11) Titov, A. V.; Mitrushenkov, A. O.; Tupitsyn, I. I. *Chem. Phys. Lett.* **1991**, *185*, 330.
(12) Tupitsyn, I. I.; Mosyagin, N. S.; Titov, A. V. *J. Chem. Phys.* **1995**, *103*, 6548.
(13) Wildman, S. A.; DiLabio, G. A.; Christiansen, P. A. *J. Chem. Phys.* **1997**, *107*, 9975.
(14) Dyall, K. G.; Enevoldsen, T. *J. Chem. Phys.* **1999**, *111*, 10000.
(15) Bonifacic, V.; Huzinaga, S. *J. Chem. Phys.* **1974**, *60*, 2779; *J. Chem. Phys.* **1975**, *62*, 1507.
(16) Leasure, S. C.; Martin, T. P.; Balint-Kurti, G. G. *J. Chem. Phys.* **1984**, *80*, 1186.
(17) Lee, Y. S.; Ermler, W. C.; Pitzer, K. S. *J. Chem. Phys.* **1977**, *67*, 5861.

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