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Authors
Smallwood, C J
Larsen, R E
Glover, W J
et al.

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A computationally efficient exact pseudopotential method. I. Analytic reformulation of the Phillips-Kleinman theory

C. Jay Smallwood, Ross E. Larsen, William J. Glover, and Benjamin J. Schwartz[a)]
Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569

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Even with modern computers, it is still not possible to solve the Schrödinger equation exactly for systems with more than a handful of electrons. For many systems, the deeply bound core electrons serve merely as placeholders and only a few valence electrons participate in the chemical process of interest. Pseudopotential theory takes advantage of this fact to reduce the dimensionality of a multielectron chemical problem: the Schrödinger equation is solved only for the valence electrons, and the effects of the core electrons are included implicitly via an extra term in the Hamiltonian known as the pseudopotential. Phillips and Kleinman (PK) [Phys. Rev. **116**, 287 (1959)]. demonstrated that it is possible to derive a pseudopotential that guarantees that the valence electron wave function is orthogonal to the (implicitly included) core electron wave functions. The PK theory, however, is expensive to implement since the pseudopotential is nonlocal and its computation involves iterative evaluation of the full Hamiltonian. In this paper, we present an analytically exact reformulation of the PK pseudopotential theory. Our reformulation has the advantage that it greatly simplifies the expressions that need to be evaluated during the iterative determination of the pseudopotential, greatly increasing the computational efficiency. We demonstrate our new formalism by calculating the pseudopotential for the 3s valence electron of the Na atom, and in the subsequent paper, we show that pseudopotentials for molecules as complex as tetrahydrofuran can be calculated with our formalism in only a few seconds. Our reformulation also provides a clear geometric interpretation of how the constraint equations in the PK theory, which are required to obtain a unique solution, are themselves sufficient to calculate the pseudopotential.
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I. INTRODUCTION

In principle, quantum mechanics is not hard; after all, it requires solving only a single well-defined equation: the Schrödinger equation. Yet, for systems where more than a few electrons are involved, even high-power computers cannot manage to solve this equation exactly. Therefore, to make computational progress on many-electron systems, it is imperative to find accurate methods for reducing the number of electronic degrees of freedom. One of the most common reduction methodologies is to differentiate between core electrons and valence electrons. Broadly defined, the core electrons are those low-energy electrons that remain relatively static during most chemical processes and act essentially as placeholders; by extension, the valence electrons are those that actively participate in chemical structure and dynamics. The specific way in which the separation between valence and core electrons is determined depends on the system of interest. For atoms and molecules, the valence electrons would be those in the highest energy shell and the remaining electrons would be the core electrons. For solids, the valence electrons would be those that contribute to the valence and conduction bands and the core electrons would be those that remain fixed to the atomic centers. For the scattering of an electron off a closed-shell molecule, the valence electron would be the scattered electron and the core electrons would be all the electrons bound to the molecule.

Given a particular choice of valence and core electrons, our goal is to develop a means to exclude the core electrons from the explicit calculation of the valence electron wave function. However, to accurately calculate the properties of the valence electrons, some implicit information related to the presence of the core electrons must be retained. Regardless of how this is accomplished, the quality of the calculated valence wave function depends on how well the implicitly included core electron information approximates the true many-electron potential in the region of interest. One common method for approximating the contribution of the core electrons to the valence electron wave function is to use a pseudopotential.[1,2] There are two major strains of pseudopotential theory,[1] model potentials and Phillips-Kleinman (PK)-type potentials. Model potentials are generally not derived from a set of well-defined postulates but are adjusted empirically or semiempirically to reproduce the desired properties of the system, e.g., the valence electron energies. In contrast, PK pseudopotentials, which are used in a variety of fields (see, e.g. Refs. 3–6), are based on a rigorously derivable quantum mechanical formalism, although such pseudopotentials are still typically calculated approximately, for example, by neglecting exchange terms.[7] In fact, as far as we are aware, there are no reports of *exact* PK pseudopotentials be-

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[a)] Electronic mail: schwartz@chem.ucla.edu ing calculated even for small molecules; up until now, application of the exact PK theory has been restricted to atoms.[1,8–12]

The reason that exact PK pseudopotentials have not been calculated for molecular systems is that such calculations have been expensive enough that additional approximations are required, often making the model approach more desirable. The challenge of building accurate model potentials, in turn, is that they require good intuition for the electronic wave functions. For atoms, the core wave functions are relatively simple and well understood; thus, very accurate models can be created, and many of these have found utility in solid-state calculations.[2] For molecules, however, the same level of intuitive knowledge is usually not available due to the complexity and variety of molecular wave functions. Since the model approach becomes increasingly less reliable for more complex systems, there is clearly a need to extend the analytically rigorous PK pseudopotential theory to systems that it currently cannot handle.

In this paper, we introduce an analytically exact reformulation of the standard PK pseudopotential theory that not only provides a large reduction in computational effort but also is more physically transparent. As we will show below, our formulation allows the calculation of exact PK pseudopotentials without the need to evaluate the computationally expensive potential energy operator. The rest of this paper is organized as follows: First, a brief discussion of PK pseudopotential theory will be given in Sec. II A. In Sec. II B, we will present our new computationally efficient pseudopotential formalism and provide a geometric interpretation of how the new equations furnish a rigorous effective potential. In Sec. II C, we discuss the computational implications of our reformulated pseudopotential theory. In Sec. III, we demonstrate the practicality of the new formalism by computing the pseudopotential for the interaction of a valence electron with a sodium cation. We finish with a few concluding remarks in Sec. IV, and we demonstrate explicitly the connection of our new formalism to the earlier work of Cohen and Heine[8] in the Appendix. In the subsequent paper, we work through the details of some of the implementation issues and demonstrate the efficiency of our new formalism by calculating the exact PK pseudopotential for an excess electron interacting with a molecule of tetrahydrofuran.

II. A NEW, EXACT PSEUDOPOTENTIAL FORMALISM FOR OBTAINING UNIQUE PSEUDO-ORBITAL SOLUTIONS

To place our work in context, in Sec. II A we present a derivation of the PK pseudopotential formalism, which can be applied to any system where the core/valence electron separation is a good approximation. We will focus our discussion on the development of the pseudopotential for the case of only one valence electron, but the formalism can be extended to treat multiple valence electrons in a straightforward manner (see, e.g., Ref. 1 and references therein). We introduce and provide a geometric interpretation of our new formalism in Sec. II B, and we conclude this section by discussing the computational advantages gained through our reformulation in Sec. II C

A. Basic PK pseudopotential theory

For a given multielectron Hamiltonian [e.g., the Hartree-Fock (HF) Hamiltonian], $\hat{H}=\hat{T}+\hat{U}$, where $\hat{T}$ is the kinetic energy operator and $\hat{U}$ is the potential energy operator, the core electron wave functions (of which there are ncore) are defined by the Schrödinger equation

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle \quad (i=1,\text{ncore}). \tag{1}$$

The valence electron wave function for this same Hamiltonian is given by

$$\hat{H}|\psi_v\rangle = \epsilon|\psi_v\rangle. \tag{2}$$

Of course, the valence electron wave function is orthogonal to all of the core electron wave functions ($\langle\psi_v|\psi_i\rangle=0$ for all i), and this orthogonality must always be preserved, even if the core electrons are no longer treated explicitly. One way to guarantee this orthogonality is to write the valence electron wave function in a basis set that is *a priori* orthogonalized to the core electrons. This *preorthogonalization* is the foundation of pseudopotential theory. Using this idea, we can orthogonalize any arbitrary basis set $\{|f_n\rangle\}$ to the core electron wave functions by defining

$$|\chi_n\rangle = |f_n\rangle - \sum_{i=1}^{\text{ncore}} \langle\psi_i|f_n\rangle|\psi_i\rangle, \tag{3}$$

where each member of the new basis set, $\{|\chi_n\rangle\}$, satisfies $\langle\chi_n|\psi_i\rangle=0$ for each $|\psi_i\rangle$. The valence electron wave function can then be expressed as a linear combination of the states in the new basis set,

$$|\psi_v\rangle = \sum_n c_n|\chi_n\rangle. \tag{4}$$

Using the definition of the preorthogonalized $\{|\chi_n\rangle\}$ above, we can reexpress Eq. (4) as

$$|\psi_v\rangle = |\phi\rangle - \sum_{i=1}^{\text{ncore}} |\psi_i\rangle\langle\psi_i|\phi\rangle \equiv |\phi\rangle - \hat{\Omega}|\phi\rangle, \tag{5}$$

where we have introduced the projection operator onto the set of core electrons wave functions, $\hat{\Omega}$,

$$\hat{\Omega} = \sum_{i=1}^{\text{ncore}} |\psi_i\rangle\langle\psi_i|, \tag{6}$$

and a new function that results from a linear combination of the $|f_n\rangle$, designated the pseudo-orbital,

$$|\phi\rangle = \sum_n c_n|f_n\rangle. \tag{7}$$

This approach of describing the valence electron wave function in a preorthogonalized basis set has been studied and used extensively as a computational tool.[13] It took the insight of Phillips and Kleinman,[14] however, to note that the geometrical constraint of preorthogonalization to the core wave functions could be expressed as an additional repulsive potential, called the pseudopotential, and that the pseudo-orbital $|\phi\rangle$ has an important physical interpretation. To derive an equation for the pseudopotential, we can substitute Eq. (5) into Eq. (2), resulting in a *one-electron* equation for $|\phi\rangle$,

$$\hat{H}|\phi\rangle + \sum_{i=1}^{\text{ncore}} (\epsilon - \epsilon_i)\langle\psi_i|\phi\rangle|\psi_i\rangle = \epsilon|\phi\rangle. \tag{8}$$

This equation has the form of our original valence eigenequation [Eq. (2)], but with an extra term arising from the preorthogonalization. This extra term, the pseudopotential, $\hat{V}_p \equiv \Sigma_{i=1}^{\text{ncore}}(\epsilon-\epsilon_i)|\psi_i\rangle\langle\psi_i|$, is a nonlocal operator, and the pseudo-orbital $|\phi\rangle$ is an eigenstate of the new effective Hamiltonian, $\hat{H}+\hat{V}_p$. In this paper, we refer to the pseudopotential strictly as the additional term $\hat{V}_p$, and we use the term "effective Hamiltonian" to refer to the original Hamiltonian plus the pseudopotential. Equation (8) shows that the pseudo-orbital has the same eigenenergy ϵ as the valence electron; moreover, this eigenenergy is the lowest in the spectrum of the effective Hamiltonian (i.e., the core energies have been removed). Even though the pseudopotential is a nonlocal operator, $\hat{V}_p$ can easily be localized, resulting in a potential that is completely defined by a single spatial coordinate:

$$V_p^{\text{local}}(\mathbf{r}) = \frac{\langle\mathbf{r}|\hat{V}_p|\phi\rangle}{\langle\mathbf{r}|\phi\rangle}. \tag{9}$$

As we will discuss further below, because the pseudo-orbital is a nonunique ground state solution of the effective Hamiltonian, it can be constructed to be nodeless, thereby avoiding any numerical problems with singularities in the pseudopotential.

The PK pseudopotential formalism thus provides a method to solve the reduced electron problem by adding a *local* potential to the original Hamiltonian that guarantees that the valence electron wave function is orthogonal to the (now implicitly treated) core electron wave functions. As can be seen in Eq. (5), $|\phi\rangle \rightarrow |\psi_v\rangle$ in regions where $|\phi\rangle$ does not overlap with the $|\psi_i\rangle$'s, that is, outside the core. Therefore, the PK pseudopotential formulation allows for an accurate calculation of the valence electron wave function as long as the specific details of the valence electron wave function inside the core region are not important, as is true for most chemical and materials applications. [For cases where more detail is required, precise information about the valence wave function in the core region always can be backed out of $|\phi\rangle$ using Eq. (5).] Inside the core, the nodeless $|\phi\rangle$ is much smoother than the true valence wave function. A detailed analysis[1] shows that the effective potential energy of the valence electron in the core region is largely constant because the attractive nuclear Coulomb potential essentially is canceled by the large kinetic energy of the valence electron, which results from the high-frequency oscillations required to orthogonalize it to the core wave functions. Thus, the use of a smooth wave function in the region of the core can be intuitively justified if the preorthogonalization is equivalent to adding an additional repulsive potential to balance the nuclear attraction; Phillips and Kleinman proved this equivalence.[14] Indeed, this cancellation is a hallmark of the pseudopotential method, as demonstrated explicitly by Cohen and Heine.[8] The net result is that Eq. (8) can be used to find a reduced-dimensionality solution for the valence electron wave function that remains orthogonal to the core electrons.

B. A new formalism for the calculation of exact PK pseudo-orbitals

We begin discussion of our new formalism by noting that there exists a formal ambiguity in the solutions to the PK pseudo-orbital expression [Eq. (8)]. By removing this ambiguity, we will arrive at an equation for a unique PK pseudo-orbital that is much more computationally efficient to evaluate than the original PK equation.[8] We then provide a geometric interpretation as to why our new formalism is sufficient to calculate exact PK pseudopotentials.

1. Derivation of the fundamental pseudo-orbital equation

In the PK theory, the solution $|\phi\rangle$ of Eq. (8) is not unique.[8] This is because for any solution $|\phi\rangle$, the function $|\phi'\rangle$, defined by

$$|\phi'\rangle = |\phi\rangle + \sum_{i=1}^{\text{ncore}} a_i|\psi_i\rangle \equiv |\phi\rangle + |\delta\phi\rangle, \tag{10}$$

is also a solution of Eq. (8) for arbitrary a_i. As Cohen and Heine pointed out, to construct a unique pseudo-orbital, one can apply an additional constraint without affecting the physics of the problem. If we choose our constraint to extremize the expectation value, $\bar{F}$, of an arbitrary observable $\hat{F}$, given by

$$\bar{F} = \frac{\langle\phi|\hat{F}|\phi\rangle}{\langle\phi|\phi\rangle}, \tag{11}$$

then the first variation[15] of this expectation value, $\delta\bar{F}$, is

$$\delta\bar{F}\langle\phi|\phi\rangle = \langle\delta\phi|\hat{F}-\bar{F}|\phi\rangle + \text{c.c.}, \tag{12}$$

and extremizing the first variation of $\hat{F}$ gives

$$\langle\delta\phi|\hat{F}-\bar{F}|\phi\rangle = 0. \tag{13}$$

Upon substituting the allowed variation, $\langle\delta\phi| = \Sigma_{i=1}^{\text{ncore}} a_i\langle\psi_i|$, into Eq. (13), one obtains

$$\sum_{i=1}^{\text{ncore}} a_i\langle\psi_i|\hat{F}-\bar{F}|\phi\rangle = 0. \tag{14}$$

Since the a_i's are arbitrary, Eq. (14) is true if and only if

$$\langle\psi_i|\hat{F}-\bar{F}|\phi\rangle = 0, \quad i = 1, \ldots, \text{ncore}. \tag{15}$$

Equation (15) provides ncore constraints that will uniquely determine the pseudo-orbital. We can recast these constraints by multiplying each expression in Eq. (15) by its corresponding core electron wave function and summing to give

$$\sum_{i=1}^{\text{ncore}} |\psi_i\rangle\langle\psi_i|\hat{F} - \bar{F}|\phi\rangle = 0, \tag{16}$$

where Eq. (16) uniquely determines the pseudo-orbital. To see this, note that Eqs. (5) and (10) imply that

$$|\phi\rangle = |\psi_v\rangle + \sum_{i=1}^{\text{ncore}} b_i|\psi_i\rangle \tag{17}$$

is a valid PK pseudo-orbital for arbitrary b_i, as can be verified by direct substitution of Eq. (17) into Eq. (8). Therefore, to uniquely determine the pseudo-orbital, we only need a method to uniquely constrain the $\{b_i\}$'s, and Eq. (16) provides the ncore constraints required to uniquely fix the pseudo-orbital/core orbital overlaps. Thus, by solving Eq. (16), we directly obtain the $\hat{F}$-extremized PK pseudo-orbital.

We can make the importance of Eq. (16) more transparent by inserting $\hat{\Omega}|\phi\rangle = |\psi_v\rangle - |\phi\rangle$ [Eq. (5)] into Eq. (16) and rearranging to get

$$|\phi\rangle = |\psi_v\rangle + \sum_{i=1}^{\text{ncore}} \frac{\langle\psi_i|\hat{F}|\phi\rangle}{\bar{F}}|\psi_i\rangle. \tag{18}$$

The solution to Eq. (18) will give an $\hat{F}$-extremized pseudo-orbital whose overlap with the core orbitals is given by

$$\langle\psi_i|\phi\rangle = \frac{\langle\psi_i|\hat{F}|\phi\rangle}{\bar{F}}. \tag{19}$$

A unique PK pseudopotential can thus be determined by using the pseudo-orbital from Eq. (18) in Eq. (9). Although Eq. (18) is a straightforward consequence of the structure of the PK theory, it in fact stands on its own as the fundamental PK pseudo-orbital equation. The identification of Eq. (18) as being sufficient to determine the constrained PK pseudo-orbital is the principal result of this work. In the Appendix, we demonstrate that Eq. (18) also encompasses the previously published pseudopotential method of Cohen and Heine.[8]

2. Discussion: A geometric interpretation of the new pseudopotential formalism

Equation (5) shows that the critical piece of information required to form the pseudo-orbital is understanding how it overlaps with the core electron wave functions. Unfortunately, there are an infinite number of ways this overlap can occur, as can be seen from Eq. (10). This is why it is impossible to construct a unique pseudopotential in the unconstrained PK formalism: Eq. (8) has an infinite number of solutions. As mentioned above, a unique solution can be found by introducing an arbitrary constraint. The fundamental pseudo-orbital expression, Eq. (18), can then be used to find a unique solution for the pseudo-orbital.

Although Eq. (18) provides a new means to solve for the unique, constrained pseudo-orbital, further examination of the ambiguity in the unconstrained $|\phi\rangle$ is fruitful. The ambiguity arises because the act of preorthogonalization (which is equivalent to writing the pseudopotential) creates a linearly dependent basis set.[8] The basis set for the original all-electron problem, $\{|f_n\rangle\}$, is linearly independent by construction, and preorthogonalization of this basis [Eq. (3)] creates a one-to-one transformation of the $\{|f_n\rangle\}$ to the respective $\{|\chi_n\rangle\}$. This process, however, involves subtracting off the overlap of the $\{|f_n\rangle\}$ with the core wave functions, but the core wave functions also depend on the $\{|f_n\rangle\}$. Thus, the preorthogonalization transformation from the $\{|f_n\rangle\}$ to the $\{|\chi_n\rangle\}$ destroys the linear independence of the basis set. A geometric interpretation is that pseudopotential theory acts to reduce the dimensionality of the all-electron Hilbert space. By preorthogonalizing the original basis set [Eq. (3)] and writing the valence electron wave function in the set of preorthogonalized vectors, we are by definition excluding the valence electron wave function from occupying any part of the Hilbert space spanned by the core electron eigenfunctions. In other words, we are restricting the valence electron wave function to a surface in Hilbert space that has ncore-lower dimensionality than the full multielectron wave function. However, due to the one-to-one nature of the basis transformation, we are using the same size basis set to describe this lower-dimensional space; therefore, the $\{|\chi_n\rangle\}$ must be linearly dependent.[16] This linear dependence is why the pseudo-orbital cannot be uniquely determined without additional constraints.

In order to uniquely describe the pseudo-orbital, a linearly independent set of basis states that spans the lower-dimensional space is required; this new basis is made to be linearly independent by adding the set of ncore constraint equations [Eq. (15)] to the original basis states. Moreover, as we argued above, these constraints are fundamental: The constraint equations themselves contain all of the essential physics underlying PK pseudopotential theory. It is worth noting that the form of the constraint equations is restricted to only those variations [Eq. (10)] that are also solutions to the original PK equation [Eq. (8)]. In other words, Eq. (10) tells us that we can choose *any* pseudo-orbital if it is preorthogonalized to the core wave functions: As long as the pseudo-orbital is constrained to the correct surface in Hilbert space, the choice of the reduced-dimensionality basis set is arbitrary. Since the surface geometry is completely defined by the core electron wave functions, it implicitly includes all of the information about the core electrons, so the constraint equations uniquely define how to reduce the dimensionality for the extremization of any particular operator. Thus, as long as the core electronic wave functions are known, they can be projected out exactly.

C. Practical consequences of the new formalism

The principle importance of the fact that Eq. (18) is sufficient to determine the PK pseudo-orbital is a dramatic improvement in the computational efficiency of calculating PK pseudopotentials. To begin this section, we will discuss general implementation issues involved in the calculation of PK pseudopotentials. We will then show that Eq. (18) allows the pseudo-orbital to be iteratively calculated in a computationally straightforward manner.

1. Implementation of the traditional PK pseudopotential theory

In principle, applying the PK theory requires just the set of core orbitals and the valence orbital [e.g., the HF lowest unoccupied molecular orbital (LUMO)]. Equation (18) then defines the pseudo-orbital, and thus the pseudopotential via Eq. (9). Before the advent of modern computers, however, there were two practical issues that limited the use of exact PK pseudopotentials. First, the core orbitals were not always known, prompting model potentials to be developed (see, e.g., Refs. 17 and 18) that relied on approximations to the pseudopotential in the core region. As mentioned in the Introduction, model potentials can be quite succesful for atoms but become increasingly unreliable for higher-complexity systems such as molecules. Fortunately, modern computational power has largely dated most concerns about obtaining full solutions to the core electron wave functions, at least for atoms and small molecules. Second, even if the core orbitals were known accurately, data on the LUMO were often absent.[19] Therefore, the PK expression [Eq. (8)] typically was solved iteratively using an initial guess of an arbitrary smooth, nodeless pseudo-orbital until self-consistency in the pseudo-orbital and its energy was achieved. The disadvantage to this scheme is that the computationally expensive two-electron integrals arising from the many-electron Hamiltonian must be evaluated at every iteration. As a result, the only published applications of PK theory solved in this way that we are aware of are for atoms.[1,10–12] [We note that, in principle, the iterative evaluation of the two-electron integrals could be avoided by expressing the pseudo-orbital in a basis. Solving the PK equation, $(\hat{H}+\hat{V}_p)|\phi\rangle=\epsilon|\phi\rangle$, could then be sped up by evaluating the matrix elements of $\hat{H}+\hat{V}_p$ before iteration. However, to our knowledge, such a procedure has not been published and its numerical stability has not been explored.]

2. Computational advantages of the new PK formalism

Although application of the traditional PK pseudopotential theory has been hampered by computational intractability, our new formalism presents a significant computational improvement. The advantage of our constrained pseudopotential formulation is that it allows the pseudo-orbital to be calculated without the need to iteratively evaluate any two-electron integrals. For example, by choosing the kinetic-energy-minimized pseudo-orbital, $\hat{F}=\hat{T}$ [Eq. (A7)], Eq. (18) avoids any explicit calculation of the potential energy operator with its multielectron integrals. Even though the pseudo-orbital must still be evaluated self-consistently, avoiding numerical evaluation of the two-electron integrals sidesteps the major computational bottleneck in computing exact PK pseudopotentials, and due to the iterative nature of solving the equation, the computational savings are multiplied. Once the pseudo-orbital has been calculated by solving Eq. (18), it is straightforward to calculate the pseudopotential, $V_p(\mathbf{r})$, using our new formalism.

For most applications, however, only the total effective potential, $\hat{U}_{\text{eff}}=\hat{U}+\hat{V}_p$, rather than the isolated pseudopotential, is needed. Since $\hat{H}=\hat{T}+\hat{U}$ and the pseudo-orbital is nodeless, we can easily obtain the localized effective potential $U_{\text{eff}}^{\text{local}}$ from[1]

$$U_{\text{eff}}^{\text{local}}(\mathbf{r})=\frac{\langle\mathbf{r}|(\epsilon-\hat{T})|\phi\rangle}{\langle\mathbf{r}|\phi\rangle}. \tag{20}$$

Thus, by choosing kinetic energy minimization, we not only have avoided the iterative calculation of the troublesome two-electron terms to determine the pseudo-orbital but we also can find the local effective potential without ever having to explicitly calculate the potential energy. Of course, information about the potential energy is implicitly included within the core electron wave functions, but once the core electron solutions are found, the construction of the effective potential does not require any additional potential energy evaluations. Because kinetic energy minimization allows for the complete exclusion of the potential energy operator, it is difficult to imagine that any other choice of $\hat{F}$ could provide a more efficient route to calculating $U_{\text{eff}}^{\text{local}}(\mathbf{r})$. But regardless of the choice of $\hat{F}$, Eqs. (18) and (20) provide a new operational method for calculating the exact pseudo-orbital and effective potential.

In the next section, we apply our new formalism, Eqs. (18) and (20), to determine the effective potential for the interaction of a single valence electron with a sodium cation, and we discuss the computational methods that are required to solve Eq. (18) numerically. In the following paper,[20] we discuss several important implementation issues of this formalism for the calculation of pseudopotentials for large, complex molecules. In particular, we apply our formalism to calculate the effective potential between an excess electron and tetrahydrofuran (THF) molecule, which, as far as we are aware, is now the most complicated molecule for which an exact pseudopotential has been determined. One particularly critical issue is that the stability of the numerical solution of Eq. (18) is sensitive to the choice of computational methodology.[20] However, with an appropriate implementation, the numerical solution of Eq. (18) is computationally trivial: Once the core and valence wave functions were determined, calculation of the excess electron-THF effective potential via Eqs. (18) and (20) took less than 3 s on a single 1.3 GHz Athlon AMD processor.[20]

III. EXAMPLE: PSEUDO-ORBITAL AND PSEUDOPOTENTIAL FOR THE SODIUM VALENCE ELECTRON

To demonstrate that our newly developed formalism [Eqs. (18) and (20)] can be used to efficiently calculate exact PK pseudopotentials, we have calculated a kinetic-energy-minimized pseudo-orbital and the corresponding localized effective potential for the 3*s* valence electron of a sodium atom. This particular atom was chosen because it has both a single valence electron and a relatively hard core (Na^+), so that we can apply the so-called frozen core approximation. The frozen core approximation assumes that the presence of the valence electron has no effect on the core eigenstates;

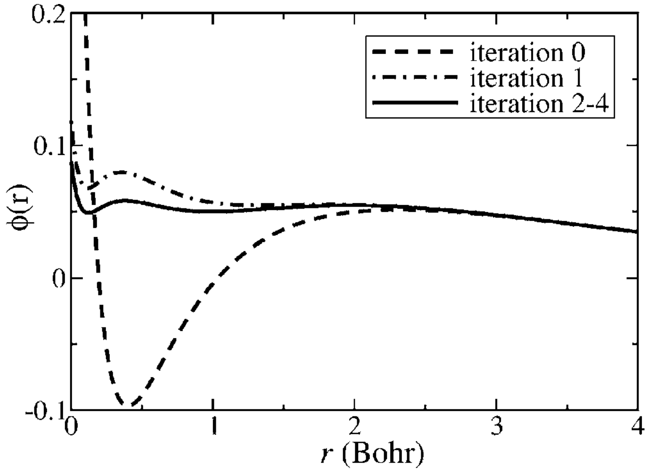

FIG. 1. Convergence of the calculated kinetic-energy-minimized sodium pseudo-orbital for the initial guess $|\phi\rangle = |\psi_{3s}\rangle$. The dashed curve shows the Na^+ LUMO (3*s*) initial guess used in the iterative solution of Eq. (21) and the other curves show the solution after the indicated number of iterations. Within four iterations the solution had converged such that $\sqrt{\langle \phi_{\text{new}} - \phi_{\text{old}} | \phi_{\text{new}} - \phi_{\text{old}} \rangle} \leqslant 10^{-14}$.

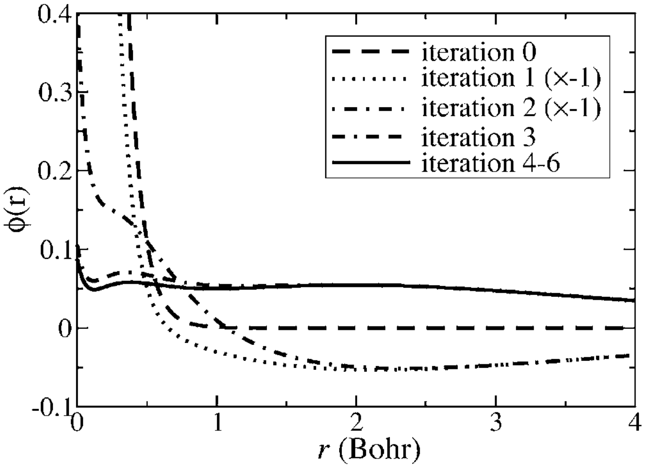

FIG. 2. Convergence of the calculated kinetic-energy-minimized sodium pseudo-orbital for the initial guess $|\phi\rangle = |\psi_{1s}\rangle$. The dashed curve shows the Na^+ 1*s* initial guess used in the iterative solution of Eq. (21) and the other curves show the solution after the indicated number of iterations. Within six iterations the solution had converged such that $\sqrt{\langle \phi_{\text{new}} - \phi_{\text{old}} | \phi_{\text{new}} - \phi_{\text{old}} \rangle} \leqslant 10^{-14}$. The solutions after iterations 1 and 2 are multiplied by −1 for clarity.

therefore, the core eigenstates computed in the presence of the valence electron are identical to those calculated in the absence of the valence electron.

To solve Eq. (18), we require the HF core and LUMO (valence) orbitals for the sodium atom in the absence of its valence electron; i.e., we need the orbitals of Na^+. These orbitals were generated from a restricted HF calculation of Na^+ using GAUSSIAN 03 Revision C.02 (Ref. 21) with a quadruple-zeta Gaussian-type orbital (GTO) basis.[22] Using this basis, the HF total energy was calculated to be −161.676 942 hartree, near the numerical HF value of −161.676 963 hartree;[23] the LUMO energy was calculated to be −0.181 801 hartree, near the frozen core numerical HF value of −0.181 802 hartree.[24] Although GTOs are perhaps not the best choice of basis to represent atomic orbitals since they cannot recreate nuclear cusps or the correct long distance asymptotic exponential behavior,[25] they are the most efficient basis to use in molecular calculations, and their use in this simple atomic pseudopotential calculation presents a test of their applicability in calculating molecular pseudopotentials.

To solve Eq. (18) we found that (even for complex molecules[20]) we could achieve a stable numerical solution for the pseudo-orbital using an iterative matrix-inversion scheme to solve

$$|\phi\rangle = \left[I - \frac{\hat{\Omega}\hat{T}}{\bar{T}} \right]^{-1} |\psi_v\rangle \equiv \hat{M}^{-1}|\psi_v\rangle, \qquad (21)$$

which is a rearranged version of Eq. (18), where $\hat{T}$ is the kinetic energy operator and where $\hat{\Omega} = \Sigma_{i=1}^{\text{ncore}} |\psi_i\rangle\langle\psi_i|$ is the projection operator onto the occupied core MOs [Eq. (6)]. To iteratively solve Eq. (21), we expanded the matrix in terms of our contracted Gaussian basis set, computed the average kinetic energy $\bar{T}$ using an initial guess for the pseudo-orbital, and solved the linear matrix equation $\hat{M}|\phi\rangle = |\psi_v\rangle$ using LAPACK routines.[26] The resulting coefficients for $|\phi\rangle$ in the contracted Gaussian basis were then used to form the matrix $\hat{M}$ for the next iteration. [Note that because of the need to iteratively solve Eq. (21), the above matrix inversion is only formal; by using the previous step's approximate pseudo-orbital to form $\hat{M}$, only the linear matrix equation needs to be solved on each iteration.]

Figures 1 and 2 show that the iterative matrix-inversion method embodied in Eq. (21) converged to the pseudo-orbital in just a few iterations regardless of the choice of initial guess. Figure 1 shows the solution of Eq. (21) after the indicated number of iterations for a starting guess of $|\phi\rangle = |\psi_{3s}\rangle = |\psi_v\rangle$, which by construction is equal to the pseudo-orbital everywhere but inside the core. Figure 2 displays the same information for a starting guess that is quite different from the final pseudo-orbital everywhere, $|\phi\rangle = |\psi_{1s}\rangle$. With either starting guess, the pseudo-orbital was found within a few iterations. The overlap integrals of the pseudo-orbital with the core orbitals, which uniquely define the pseudo-orbital via Eq. (5), were calculated to be $\langle \psi_{1s} | \phi \rangle = 0.023\,487\,39$ and $\langle \psi_{2s} | \phi \rangle = 0.227\,198\,0$; by construction [cf. Eq. (18) and see Ref. 27], $\langle \psi_{3s} | \phi \rangle = 1$. A comparison of the converged PK pseudo-orbital (solid curve) and the valence orbital (dashed curve) displayed in Fig. 1 shows that the pseudo-orbital exhibits the features we desire: It is nodeless, much smoother than the valence orbital, and exactly matches the valence orbital in the region outside the core.

Once the pseudo-orbital was calculated, we generated the localized effective potential for the sodium atom using Eq. (20), as shown in Fig. 3. This effective potential

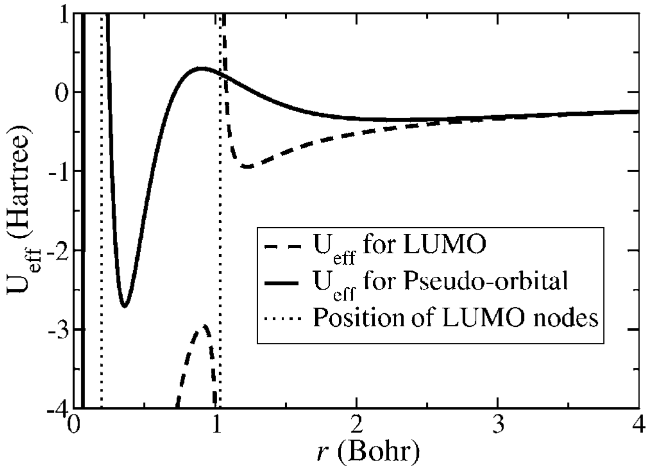

FIG. 3. Kinetic-energy-minimized PK effective potential for the valence electron/Na$^+$ interaction. The dashed curve shows the effective potential for the LUMO calculated via Eq. (20) for $|\phi\rangle = |\psi_{3s}\rangle$ (the orbital displayed as a dashed curve in Fig. 1); i.e., this curve is the Na$^+$ LUMO HF potential, which for clarity is shown only for $r > 0.5$ a.u. The vertical dotted lines indicate singularities in the LUMO HF potential (where the LUMO has radial nodes). The kinetic-energy-minimized PK effective potential, which has no singularities, is shown by the solid curve.

(solid curve) also demonstrates the features we desire: It is less attractive than the HF potential $\hat{U}$ (i.e., the effective potential for the LUMO; dashed curve) in the core region due to the contribution from the repulsive pseudopotential $\hat{V}_p$ that accounts for the energetic cost of orthogonalizing the valence orbital to the core orbitals. In addition, outside the core, $\hat{U}_{\rm eff}$ approaches the HF potential, as expected.[25]

To our knowledge, no kinetic-energy-minimized (Cohen-Heine,[8] see the Appendix) atomic pseudo-orbital or pseudopotential for the Na atom 3*s* valence electron has been previously published; however, Szasz and McGinn[10] calculated an unconstrained PK pseudo-orbital for sodium by iteratively solving Eq. (8) with an initial pseudo-orbital guess of the ground state solution to the Hellmann potential (i.e., a smooth pseudo-orbital); their nonunique solution to Eq. (8) therefore should be close to a rigorously kinetic-energy-minimized PK pseudo-orbital. Indeed, there is close agreement between our Figs. 1 and 3 and Figs. 1 and 2 of Ref. 10.

Finally, we note that the kinetic-energy-minimized effective potential shown in Fig. 3 varies rapidly in the core region; in many applications, such sharp variations may need to be smoothed out. One cannot simply smooth the effective potential, however, because solutions of Schrödinger's equation with such a potential will not necessarily have the correct energy or shape. Instead, one must first smooth the *pseudo-orbital* and insert the smoothed pseudo-orbital into Eq. (20) to produce a slowly varying effective potential. By smoothing the potential in this fashion, one guarantees by construction that the resulting pseudo-orbital will have the correct energy and shape.

IV. CONCLUSIONS

In summary, we have presented an analytically exact reformulation of the Phillips-Kleinman pseudopotential theory; as shown in the Appendix, our reformulated theory is formally the same as that of Cohen and Heine for certain choices of extremization. Our formalism has the advantage of furnishing a clear geometric interpretation, but its real importance lies in its computational efficiency. We expect that the use of Eqs. (18) and (20) will allow for the rigorous computation of complex pseudopotentials that cannot be well represented by model potentials and that currently lie on the edge of computational practicality. In fact, computation of the pseudopotential for large molecules will no longer be limited by solving the iterative pseudopotential equation, but instead by the generation of the core electron and LUMO wave functions for large multielectron systems. In the subsequent paper,[20] we will apply our method to calculate the effective potential for an excess electron interacting with a molecule of tetrohydrofuran (THF). This is now the largest molecule for which an exact pseudopotential has been calculated and, as we discuss in more detail in Ref. 20, lies well on the low end of computational feasibility.

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APPENDIX: EQUIVALENCE OF THE NEW FORMALISM TO THE METHOD OF COHEN AND HEINE

As described in the text, the variational flexibility of the solutions to the PK pseudo-orbital equation [Eq. (8)] and the consequent freedom to fix the potential by implementing additional constraints also have been explored previously by Cohen and Heine.[8] What we demonstrate in this appendix is that Cohen and Heine's equations, although they produce the correct constrained PK pseudo-orbital, are formally equivalent to solving Eq. (18) alone. To make this equivalence clear, we begin by rederiving the Cohen-Heine equations using a slight modification of their original approach. In their paper,[8] Cohen and Heine use the constraints of Eq. (16) to derive a set of PK-type pseudo-orbital equations via direct substitution for the specific cases of $\hat{F} = \hat{T}$ and $\hat{F} = \hat{U} + V_p$. Here, we will derive Cohen and Heine's equations for the general constraint operator $\hat{F}$, and by doing so, we will prove their equivalence to Eq. (18).

We start by noting that using Eq. (2), Eq. (8) can be rewritten as

$$\hat{H}|\phi\rangle + \sum_{i=1}^{\rm ncore} |\psi_i\rangle\langle\psi_i|\epsilon - \hat{H}|\phi\rangle = \epsilon|\phi\rangle. \tag{A1}$$

We can then add zero to Eq. (A1) in the form of Eq. (16), giving

$$\hat{H}|\phi\rangle + \sum_{i=1}^{\rm ncore} |\psi_i\rangle\langle\psi_i|\epsilon - \hat{H}|\phi\rangle + \sum_{i=1}^{\rm ncore} |\psi_i\rangle\langle\psi_i|(\hat{F} - \bar{F})|\phi\rangle$$
$$= \epsilon|\phi\rangle. \tag{A2}$$

Next, using the linearity of $\hat{\Omega}$ [Eq. (6)], we can obtain Cohen and Heine's PK-type equation for the pseudo-orbital with a generalized constraint,

$$\hat{H}|\phi\rangle + \sum_{i=1}^{\text{ncore}} |\psi_i\rangle\langle\psi_i|\epsilon - \hat{H} + (\hat{F} - \bar{F})|\phi\rangle = \epsilon|\phi\rangle. \tag{A3}$$

The (nonlocal) pseudopotential operator with a generalized constraint using the pseudo-orbital found from Eq. (A3) is then given by

$$\hat{V}_p = \hat{\Omega}[\epsilon - \hat{H} + (\hat{F} - \bar{F})]. \tag{A4}$$

When kinetic energy minimization is used, the choice $\hat{F}=\hat{T}$ leads to a cancellation with the kinetic energy operator in the Hamiltonian, resulting in the pseudopotential equation

$$\hat{H}|\phi\rangle + \hat{\Omega}(\epsilon - \hat{U} - \bar{T})|\phi\rangle = \epsilon|\phi\rangle. \tag{A5}$$

Equation (A5) is identical to that derived by Cohen and Heine;[8] this expression has been used as a starting point, along with additional approximations, to calculate pseudopotentials in several examples in the literature. A common approximation has been to neglect the $\hat{\Omega}(\epsilon-\bar{T})$ terms in Eq. (A5), removing the need to solve self-consistently; Cohen and Heine[8] calculated the expectation value of this neglected term and found it to be small in comparison to $\langle\hat{\Omega}\hat{U}\rangle$, at least for the pseudo-orbital of Si^{4+}. Another common approximation has been to assume that the pseudo-orbital is constant over the region of space where the core orbitals have amplitude, thereby simplifying the operation of the core projection operator.[7,17] In their study of F centers in alkali halides, Kübler and Friauf[28] used both of the above approximations, in addition to using an analytic approximation to the Hartree potential and neglecting exchange. More recently, Turi and Borgis[29] generated a kinetic-energy-minimized pseudo-orbital for a water molecule and used it to construct a model potential for an excess electron interacting with water by varying the model potential until the ground state wave function of the effective Hamiltonian was as close as possible to the pseudo-orbital.

It is important to note, however, that in the derivation of Eq. (A5), it is assumed that the pseudo-orbital has the form of Eq. (5). But as we saw in the text in the derivation of Eq. (17), *any* pseudo-orbital of the form of Eq. (5) will be a solution to Eq. (A1). Therefore, the first two terms on the left-hand side of Eq. (A2) are guaranteed to cancel with the term on the right-hand side no matter what the choice of the constraint. When these terms are subtracted off, all that remains is the expression for the constraints [Eq. (18)], which as we argued in the text, is sufficient to determine the pseudo-orbital for any chosen extremization, provided that $|\psi_v\rangle$ is known. Thus, we see that in their approach, Cohen and Heine, by canceling terms in the pseudopotential part [Eq. (A4)] of Eq. (A3), obscured the actual expression that needs to be solved. Overall, the use of the Cohen-Heine expression, Eq. (A5), requires unnecessary computational effort to calculate terms that analytically sum to zero. Thus, previous work based on the Cohen-Heine expression did indeed calculate the correct kinetic-energy-minimized pseudopotential, but with unnecessary computational expense.

For completeness, we close this section by explicitly demonstrating the equivalence of the Cohen-Heine formalism, Eqs. (A2)–(A5), to our Eq. (18) for the specific case of kinetic energy minimization, $\hat{F}=\hat{T}$. Making use of the fact that $[\hat{\Omega},\hat{H}]=0$, which implies that $\hat{\Omega}\hat{U}=\hat{T}\hat{\Omega}-\hat{\Omega}\hat{T}+\hat{U}\hat{\Omega}=\hat{H}\hat{\Omega}-\hat{\Omega}\hat{T}$, Eq. (A5) can be rewritten as

$$(\hat{H}-\epsilon)(|\phi\rangle - \hat{\Omega}|\phi\rangle) - \bar{T}\hat{\Omega}|\phi\rangle + \hat{\Omega}\hat{T}|\phi\rangle = 0. \tag{A6}$$

We can now substitute Eq. (5) into Eq. (A6) and make use of Eq. (2) to obtain

$$|\phi\rangle = |\psi_v\rangle + \sum_{i=1}^{\text{ncore}} \frac{\langle\psi_i|\hat{T}|\phi\rangle}{\bar{T}}|\psi_i\rangle, \tag{A7}$$

which is just Eq. (18) with $\hat{F}=\hat{T}$. It is worth emphasizing that pseudo-orbital solutions obtained from either Eq. (A3) or (A5) are perfectly correct; Eq. (A5) is just unnecessarily numerically complex in comparison to the equivalent equation (18).

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to slightly increase the amount of pseudocharge density in the core region relative to outside the core. So-called norm-conserving pseudopotentials (Ref. 30) correct for this behavior; however, they are not based on the rigorously derivable PK theory.

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