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A Note on an Aspect of Pseudopotential Theory

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The variational approach of Rice and Weeks [J. chem. physics **49**, 2741 (1968)] is used to derive the pseudopotential equation for the *T*-matrix, via a discussion of normal perturbation theory.

1. Introduction

It has long been recognized that for atoms, molecules and solids, the rather complicated situation wherein all particles move under the mutual influence of all others, can be approximated, quite accurately, by reasonably simple descriptions. The hartree-fock method, for example, is just such a description, and many useful observations have been derived from it. In particular, it has been found that for a valence electron inside the core of an atom, there is almost complete cancellation between its kinetic and potential energies [1–4]. This suggests that the original equation may be replaced by an alternative which illustrates, in a somewhat more obvious way, the effect of this cancellation, and the mathematical procedure for implementing this alternative formulation is known as the method of pseudopotentials.

What Phillips and Kleinmann [1] first showed, was that the eigenvalue equation,

$$H\Psi_i = E_i\Psi_i \tag{1.1}$$

where

$$\langle\Psi_i|\Psi_j\rangle = \delta_{ij}, \quad \text{and} \quad \Psi_i \in \{\Psi_c\}, \tag{1.2}$$

for all valence electrons, could be transformed to,

$$(H + \Omega_i)\,\Phi_i = T_i\Phi_i \tag{1.3}$$

without the orthogonality constraint. The non-local pseudopotentials Ω_i, are defined by,

$$\Omega_i\Phi = \sum_c \langle\Psi_c|\Phi\rangle\,[E_i - E_c]\,|\Psi_c\rangle$$

and the summation is over the core orbitals $\{\Psi_c\}$. Subsequently, Austin, Heine, and Sham [5], following earlier work by Cohen and Heine [4], showed that the general form of the pseudopotential could be written as,

$$\Omega\Phi = \sum_c \langle g_c|\Phi\rangle\,|\Psi_c\rangle$$

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in which g_c are arbitrary functions. Weeks and Rice [6] have, in a very elegant way, derived the most general form in terms of any hermitian operator $\hat{\Theta}$, and an arbitrary set of functions which define the projection operator P, thus

$$\Omega = P\hat{\Theta} + \hat{\Theta}P - P\hat{\Theta}P - \lambda P$$

where λ is a lagrange multiplier.

As they stand, pseudopotentials are of no advantage from a computational point of view, although the insight they afford into a given problem may often be valuable. Rather, their importance lies in the model potentials they suggest – an aspect which has been exploited with success by Heine and his co-workers [8, 9], and Rice and his co-workers [6, 7] – and in this note, Rice's method is extended to the scattering problem via an examination of the effect of introducing pseudopotentials in perturbation theory.

2. Variation Principles and Pseudopotentials

Rice and Weeks [6] have pointed the way in terms of the general discussion of pseudopotential theory and its relation to variation principles. Consider a hermitian operator $\hat{\Theta}$, and some arbitrary subset $\{\phi_c\}$ of the complete set of orthogonal functions that span its function space. The projection operator P defined in terms of the subset $\{\phi_c\}$ by,

$$P = \sum_c |\phi_c\rangle \langle \phi_c| , \tag{2.1}$$

may be used to define further a functional ω in terms of the operator $\hat{\Theta}$, a function ϕ and the subset, thus

$$\omega = \langle (1-P)\phi | \hat{\Theta} | (1-P)\phi \rangle . \tag{2.2}$$

An arbitrary variation of ϕ^*, without any constraint, leads to

$$\delta\omega = \langle \delta\phi | (1-P)\, \hat{\Theta}(1-P) | \phi \rangle , \tag{2.3}$$

since the complement of P is hermitian, so that requiring $\delta\omega = 0$ leads to

$$\Omega\phi = [P\hat{\Theta} + \hat{\Theta}P - P\hat{\Theta}P]\, \phi , \tag{2.4}$$

which is the general unconstrained pseudopotential equation. Substitution of (2.1), together with $[P, \hat{\Theta}] = 0$, leads to

$$\Omega\phi = \sum_c \langle g_c | \phi \rangle | \phi_c \rangle , \tag{2.5}$$

where

$$\langle g_c | = \langle \phi_c | \, \hat{\Theta} . \tag{2.6}$$

(2.6) is the equation suggested by Austin, Heine and Sham [5] as defining the general pseudopotential. If the variation of ω with respect to arbitrary $\phi\, (\phi^*)$ is required subject to the normalization condition,

$$\langle (1-P)\, \phi | (1-P)\, \phi \rangle = 1 , \tag{2.7}$$

then the resulting pseudopotential equation is easily seen to reduce to,

$$\Omega\phi = \sum_c \{\langle g_c|\phi\rangle - \lambda\langle\phi_c|\phi\rangle\}|\phi_c\rangle\,, \tag{2.8}$$

where λ is the appropriate lagrange multiplier. Eq. (2.8) is the generalized pseudopotential equation first derived by Rice and Weeks [6]. Setting $\hat{\Theta} = \hat{H}$, the hartree-fock hamiltonian leads to the Phillips-Kleinman equation [1], and $\hat{\Theta} = \hat{T}$ to that of Cohen and Heine [4]. Any number of $\hat{\Theta}$'s can thus be chosen to suit a variety of situations.

There has been widerspread use of these equations and their modifications [4, 5, 8, 9] in many bound-state calculations for atoms [6], molecules and solids [10–12] and more recently attention is being focused on similiar problems involving scattering [13]. Now it is well known that the transition from bound-state to unbound-state problems requires a modification of the formalism to account for the somewhat different physical situation, in which for example, the energy of the system is no longer an observable but simply a parameter. However, before considering the scattering problem in the light of Eqs. (2.5) and (2.8), it may be worthwhile to see what influence the introduction of a pseudopotential has in, say, the hartree-fock perturbation problem. At first sight the introduction of a pseudopotential in hartree-fock perturbation calculations may well seem an expedient measure, for one of the difficulties in such calculations is implementing the requirement that the perturbation equations for the different orbitals be solved subject to the overall orthogonality of the perturbed wavefunctions. Thus to second order, for example, the requirement

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}\,, \tag{2.9}$$

for the perturbed orbitals ψ_i and ψ_j leads to subsidiary conditions such as

$$\langle\psi_i^{(0)}|\psi_j^{(0)}\rangle = \delta_{ij}\,, \tag{2.10}$$

$$\langle\psi_i^{(0)}|\psi_i^{(1)}\rangle = 0\,, \tag{2.11}$$

$$\langle\psi_i^{(0)}|\psi_j^{(1)}\rangle = -\langle\psi_i^{(1)}|\psi_j^{(0)}\rangle\,, \tag{2.12}$$

$$2\langle\psi_i^{(0)}|\psi_i^{(2)}\rangle = -\langle\psi_i^{(1)}|\psi_i^{(1)}\rangle\,, \tag{2.13}$$

$$\langle\psi_i^{(2)}|\psi_j^{(0)}\rangle + \langle\psi_i^{(0)}|\psi_j^{(2)} = -\langle\psi_i^{(1)}|\psi_j^{(1)}\rangle \tag{2.14}$$

for the zero, first and second-order functions. Now the introduction of a pseudopotential transforms the equations,

$$H\psi_i = \varepsilon_i\psi_i\,, \tag{2.15}$$

subject to

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}\,,$$

to

$$(H + \Omega_i)\,\phi_i = \varepsilon_i\phi_i\,, \tag{2.16}$$

without the subsidiary conditions (2.12) and (2.14) in the perturbation problem.

Suppose, therefore, that a perturbation solution is sought to the equations,

$$(H+V)\,\psi_i = E_i \psi_i\,, \tag{2.17}$$

for the perturbed hartree-fock orbitals ψ_i. The equations for the perturbed wavefunctions are to successive order given by,

$$(H-\varepsilon_i^{(0)})\,\psi_i^{(0)} = 0\,, \tag{2.18}$$

$$(H-\varepsilon_i^{(0)})\,\psi_i^{(1)} = [\varepsilon_i^{(1)} - (V+\delta_1 V)]\,\psi_i^{(0)}\,, \tag{2.19}$$

$$(H-\varepsilon_i^{(0)})\,\psi_i^{(2)} = \varepsilon_i^{(2)}\psi_i^{(0)} + [\varepsilon_i^{(1)} - (V+\delta_2 V)]\,\psi_i^{(1)}\,, \tag{2.20}$$

etc. subject to Eqs. (2.10) to (2.14), and in which

$$\varepsilon_i^{(1)} = \langle \psi_i^{(0)} | V+\delta_1 V | \psi_i^{(0)} \rangle\,, \tag{2.21}$$

$$\varepsilon_i^{(2)} = \langle \psi_i^{(1)} | V+\delta_1 V | \psi_i^{(0)} \rangle\,, \tag{2.22}$$

and further

$$\varepsilon_i^{(3)} = \langle \psi_i^{(1)} | V+\delta_1 V | \psi_i^{(1)} \rangle\,. \tag{2.23}$$

$\delta_n V$ is the n^{th} order induced perturbation which results from the form of the hartree-fock potential. Now (2.15) may be changed to

$$(H+V+\Omega_i)\,\phi_i = \eta_i \phi_i\,, \tag{2.24}$$

in which Ω_i is any pseudopotential, and $E_i = \eta_i$ from the basic theorem. Eq. (2.24) may be grouped in two ways, either

$$[(H+\Omega_i)+V]\,\phi_i = \eta_i \phi_i\,, \tag{2.25}$$

or

$$[H+(V+\Omega_i)]\,\phi_i = \eta_i \phi_i\,, \tag{2.26}$$

in which the pseudopotential is grouped either with H, or the perturbation V. Let the perturbed pseudofunctions be denoted by $\phi_i^{(k)}$ and the corresponding energies by $\eta_i^{(k)}$, and consider first the perturbed functions which follow from the partition (2.25).

$$(H+\Omega_i)\,\phi_i^{(0)} = \eta_i^{(0)} \phi_i^{(0)}\,, \tag{2.27}$$

with $\varepsilon_i^{(0)} = \eta_i^{(0)}$. However, $\phi_i^{(0)} \neq \psi_i^{(0)}$, so that in general

$$\phi_i^{(k)} \neq \psi_i^{(k)}\,, \quad \text{for all} \quad k\,,$$

and

$$\eta_i^{(k)} \neq \varepsilon_i^{(k)}\,, \quad \text{for all} \quad k>0\,.$$

The first partition, therefore, whilst giving the same total and zero-order energies as the usual theory, gives no other correspondence between the perturbed functions and energies. Partition (2.26) on the otherhand, results in the following equations.

$$H\phi_i^{(0)} = \eta_i^{(0)} \phi_i^{(0)}\,, \tag{2.28}$$

so that $\phi_i^{(0)} = \psi_i^{(0)}$, and $\eta_i^{(0)} = \varepsilon_i^{(0)}$.

Further

$$\eta_i^{(1)} = \varepsilon_i^{(1)} .$$

However, the first-order equation is

$$(H - \varepsilon_i^{(0)})\,\phi_i^{(1)} = [\varepsilon_i^{(1)} - (V + \delta_1 V + \Omega_i)]\,\psi_i^{(0)} , \tag{2.29}$$

and similarly for higher orders. Thus, in general,

$$\phi_i^{(k)} \neq \psi_i^{(k)} , \quad \text{for} \quad k > 0$$

and

$$\eta_i^{(k)} \neq \varepsilon_i^{(k)} , \quad \text{for} \quad k > 1 .$$

For the special case of the Phillips-Kleinman potential,

$$\Omega_i \psi_i^{(0)} = 0 , \tag{2.30}$$

the k^{th} order inequalities, therefore, now become,

$$\phi_i^{(k)} \neq \psi_i^{(k)} , \quad \text{for} \quad k > 1$$

and

$$\eta_i^{(k)} \neq \varepsilon_i^{(k)} , \quad \text{for} \quad k > 3 .$$

A lack of correspondence between the actual and the pseudofunctions clearly exists, and could lead to serious discrepancies in the calculation of certain properties – a situation which is likely to be reflected in scattering problems with their formal resemblance to the usual perturbation theory.

Turning now to the formulation in scattering processes, a natural choice for the invariants around which to construct the pseudopotential theory, are the elements of the T-matrix. Such a choice is rationalized in terms of the central role played by the T-matrix in scattering, its connection with the S- and K-matrices, and its relation to the important observables in the phase-shift analysis.

Equations are sought, therefore, which leave invariant the elements T_{ba} which in the notation of Lippmann and Schwinger [14] are defined by

$$T_{ba} = \langle \phi_b, V \phi_a^+ \rangle = \langle \phi_b^-, V \phi_a \rangle . \tag{2.31}$$

The incoming and outgoing waves $\phi_a^\pm$ are defined in terms of the hamiltonian, H_0, and eigenfunctions $\{\phi_a\}$ of the initial and final states, and V the interaction operator, thus [14],

$$\phi_a^\pm = \phi_a + \frac{1}{E_a \pm i\varepsilon - H_0} V \phi_a^\pm , \tag{2.32}$$

The functional corresponding to ω for bound states, cf. Eq. (2.2), is now the Lippman-Schwinger functional τ_{ba}, defined in the present context by,

$$\begin{aligned}\tau_{ba} = \Big\{ &\langle (1-P)\,\phi_b^-, V\phi_a) + \langle \phi_b, V(1-P)\,\phi_a^+ \rangle - ((1-P)\,\phi_b^-, V(1-P)\,\phi_a^+) \\ &+ \Big\langle (1-P)\,\phi_b^-, V \frac{1}{E + i\varepsilon - H_0} V(1-P)\,\phi_a^+ \Big\rangle \Big\}\end{aligned} \tag{2.33}$$

in which the projection operator P is defined with respect to a given subset $\{\phi_c\}$ of H_0. Arbitrary variations of ϕ_a^+ and ϕ_b^- lead to,

$$\begin{aligned}\delta\tau_{ba} = \left\{\right. & \langle\delta\phi_b^-, (1-P)\,V\,\phi_a\rangle + \langle\phi_b, V(1-P)\,\delta\phi_a^+\rangle - \langle\delta\phi_b^-, (1-P)\,V(1-P)\,\phi_a^+\rangle \\ & -\langle\phi_b^-, (1-P)\,V(1-P)\,\delta\phi_a^+\rangle \\ & +\left\langle\delta\phi_b^-, (1-P)\,V\,\frac{1}{E+i\varepsilon-H_0}\,V(1-P)\,\phi_a^+\right\rangle \\ & +\left\langle\phi_b^-, (1-P)\,V\,\frac{1}{E+i\varepsilon-H_0}\,V(1-P)\,\delta\phi_a^+\right\rangle\end{aligned} \tag{2.34}$$

The condition $\delta\tau_{ba}=0$ leads to equations of the form,

$$\phi_a^+ = \phi_a + P\phi_a^+ + \frac{1}{E+i\varepsilon-H_0}\,V(1-P)\,\phi_a^+\,, \tag{2.35}$$

which may be written as,

$$\phi_a^+ = \phi_a + \left[\frac{1}{E+i\varepsilon-H_0}\,(V+\Omega_a)\right]\phi_a^+\,, \tag{2.36}$$

from which,

$$\Omega_a\phi_a^+ = [(E+i\varepsilon-H_0)-V]\,P\phi_a^+\,. \tag{2.37}$$

Writing $P=\sum\limits_c|\phi_c\rangle\,\langle\phi_c|$, and setting ε to zero, Eq. (2.37) reduces to,

$$\Omega\phi_a^+ = \sum_c\{(E-E_c)\,(\phi_c|\phi_a^+) - \langle\phi_c, V\phi_a^+\rangle\}\,|\phi_c\rangle \tag{2.38}$$

an equation which bears an obvious resemblance to the corresponding Eqs. (2.5) and (2.8). Operators defined by (2.38) clearly leave the elements of the T-matrix invariant when added to the potential V, and are therefore genuine pseudopotentials.

The approach to pseudopotentials outlined above is strictly valid for one-electron operators and wavefunctions only, and needs modification when considering the many-electron anologue. Thus the general n-electron trial function takes the form,

$$\psi(1,\ldots,N) = \prod_{i=1}^{N}(1-P_i)\,\phi(1,\ldots,N)\,, \tag{2.39}$$

with P_i defined in the usual way by,

$$P_i = \sum_c|\phi_c(i)\rangle\,\langle\phi_c(i)|\,. \tag{2.40}$$

Eq. (2.39) may be written as,

$$\psi(1,\ldots,N) = (1-Q)\,\phi(1,\ldots,N)\,,$$

in which $(1-Q)$ is idempotent, so that for the hermitian operator $\hat{\Theta}$, the n-electron pseudopotential equation is given by,

$$\Omega\phi(1,\dots,N)=\{Q\hat{\Theta}+\hat{\Theta}Q-Q\hat{\Theta}Q-\lambda Q\}\,\phi(1,\dots,N)\,. \tag{2.42}$$

Product functions $\phi_1(1),\dots,\phi_N(N)$, whether antisymmetrized or not, reduce Eq. (2.42) to the usual form when $\hat{\Theta}$ is a one-electron operator, but for two-electron operators the situation is slightly more complicated. A simple product variation function of the form,

$$\psi(1,2)=(1-Q)\,\phi(1)\,\psi(2)\,, \tag{2.43}$$

in which

$$Q=P_1+P_2-P_1P_2\,, \tag{2.44}$$

leads to the following two-electron pseudopotential equation,

$$\Omega(1,2)\,\phi(1)=[\langle\psi(2)|Q\hat{\Theta}|\psi(2)\rangle-\lambda\langle\psi(2)|Q|\psi(2)\rangle]\,|\phi(1)\rangle\,, \tag{2.45}$$

which may be expanded to,

$$\begin{aligned}\Omega(1,2)\,\phi(1)=\sum_c\,&[\langle\phi_c(1)\,\psi(2)|\hat{\Theta}(1,2)|\phi(1)\,\psi(2)\rangle-\lambda\langle\phi_c(1)|\phi_c(1)\rangle]\,|\phi_c(1)\rangle\\&+\sum_d\langle\phi_d(2)|\psi(2)\rangle\,[\langle\phi_d(2)|\hat{\Theta}(1,2)|\psi(2)\rangle\\&-\lambda\langle\phi_d(2)|\psi(2)\rangle]\,|\phi(1)\rangle\\&+\sum_{c,d}\langle\phi_d(2)|\psi(2)\rangle\,\langle\phi_c(1)|\phi(1)\rangle\,[\langle\phi_c(1)\,\phi_d(2)|\hat{\Theta}(1,2)|\phi(1)\,\psi(2)\rangle\\&-\lambda\langle\phi_d(2)|\psi(2)\rangle\,\langle\phi_c(1)|\phi(1)\rangle]\,|\phi_c(1)\rangle\,,\end{aligned} \tag{2.46}$$

and similarly for $\psi(2)$. In the calculation of the matrix elements of Ω, expansions in terms of orthogonal functions greatly simplify (2.46), and the only non-vanishing elements derive from the first summation.

For antisymmetrized products of the form,

$$\psi(1,2)=2^{-1/2}(1-P_1)\,(1-P_2)\,(\phi(1)\,\psi(2)-\psi(1)\,\phi(2))\,, \tag{2.47}$$

Eq. (2.45) is modified to include exchange, and is now given by,

$$\begin{aligned}\Omega\phi(1)=&[\langle\psi(2)|Q\hat{\Theta}|\psi(2)\rangle-\lambda\langle\psi(2)|Q|\psi(2)\rangle]\,|\phi(1)\rangle\\&-[\langle\psi(2)|Q\hat{\Theta}|\phi(2)\rangle-\lambda\langle\psi(2)|Q|\phi(2)\rangle]\,|\psi(1)\rangle\end{aligned} \tag{2.48}$$

Once again, the only non-vanishing matrix elements of involving exchange, are obtained from the expansion,

$$-\sum[\langle\phi_c(1)\,\psi(2)|\hat{\Theta}|\psi(1)\,\phi(2)\rangle-\lambda\langle\psi(2)|\phi_c(2)\rangle]\,|\phi_c(1)\rangle\,.$$

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