Pseudopotential Theory for Atoms and Molecules

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An exact pseudopotential theory is presented for atoms and molecules with arbitrary number of valence and core electrons and arbitrary number of nuclei. Using the variation method an equation is derived for the best many-valence-electron wave function which is orthogonalized to the core orbitals. Using this equation the exact equation is derived for the many-valence-electron pseudo-wavefunction which does not have to satisfy any orthogonality conditions. The Hamiltonian of the pseudopotential equation is of surprisingly simple structure and does not depend on the energy and/or on the wave function of the valence electrons. It is shown that the simple model Hamiltonian which is used in many pseudopotential calculations can be derived from the exact equation by two plausible approximations. The theory is elucidated on the example of atoms with two valence electrons.

I. Introduction

Although the powerful ab initio methods of the Quantum Chemistry the Hartree-Fock method[1] for atoms and the LCAO-MO method[2] for molecules can, in principle, be applied to any system, there are situations in which the application of the simpler pseudopotential formalism can be advantageous. The basic idea of this method – an idea which was introduced into the Quantum Chemistry by Hellmann[3] – is to replace the orthogonality requirement between valence and core wave functions by pseudopotentials and solve the Schroedinger equation for the valence electron as if the core would not exist.

The present situation in atomic and molecular pseudopotential theory may be described as follows. For one-valence-electron systems the theory has been worked out by a number of scientists among them Hellmann[3], Gombas[4], Szepfalussy[5], Phillips and Kleinmann[6], Antoncik[7], Cohen and Heine[8], Austin Heine and Sham[9], Goddard[10] and Öhrn and McWeeny[11]. Much less work has been done on the many-valence-electron formulation of the pseudopotential theory. Progress in that direction was made by Szasz[12] and by Weeks and Rice[13] who developed methods for the pseudopotential treatment of atoms with more than one valence electrons. Starting from the LCAO-MO theory Schwarz[14] contributed to the understanding of the approximations underlying the pseudopotential model Hamiltonian used in atomic and molecular calculations. Although in the most important area of applications – the molecular calculations – there is a growing number of scientists who use the pseudopotential method[15], a comprehensive many-electron pseudopotential theory up to now had not been developed. The molecular calculations[15] are usually based on physically plausible model Hamiltonians which are generalizations of the pseudopotential model for one-valence-electron systems.

The purpose of this paper is to present a comprehensive, exact, many-valence-electron pseudopotential theory for atoms and molecules. The main features of this theory are as follows:

1. The theory is comprehensive in the sense that it is applicable to atoms and molecules with any number of valence and core electrons and with any number of nuclei;

2. it is exact in the sense that the equation for the many-valence-electron wave function is derived using the variation principle and corresponds to the energy minimum;

3. the correlation effects between the valence electrons are fully taken into account.

The paper is organized as follows. First we derive the equation for the valence electron wave function which is orthogonal to the core orbitals and we discuss the structure of this equation (Section III). In Sect. IV we formulate the exact pseudopotential theory by deriving the equation for the exact pseudo-wavefunction[16]. Section IV contains also a discussion of the properties of this equation. In Sect. V we show that a simple and physically plausible model Hamiltonian which has been used in atomic and molecular calculations can be derived from the exact pseudopotential equation by just two approximations. In Sect. VI the connection between the exact theory and the model Hamiltonian is elucidated on the example of atoms with two valence electrons.

II. The Hartree-Fock Approximation

Let us consider an atom or molecule with N electrons in closed shells and arbitrary number of nuclei. In order to provide a unified treatment we write the Hamiltonian of the system in the following form:

$$H = \sum_{i=1}^{N} t_i + \tfrac{1}{2} \sum_{i,j=1}^{N} v_{ij} , \tag{2.1}$$

where v_{ij} is the electron-electron interaction and for t_i we put:

A) for atoms:

$$t_i = -\tfrac{1}{2} \Delta_i - Z/r_i , \tag{2.2}$$

where Δ_i is the Laplacian and Z the nuclear charge;

B) for molecules,

$$t_i = -\tfrac{1}{2} \Delta_i - \sum_{(a)} Z_a/r_{ai} , \tag{2.3}$$

where Z_a is the nuclear charge on nucleus "a" and r_{ai} is the electrons distance from nucleus "a".

The interaction potential between the electrons is put in the form

$$v_{12} = \langle \boldsymbol{r}_1 \boldsymbol{r}_2 | v | \boldsymbol{r}_1' \boldsymbol{r}_2' \rangle = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_1')\, \delta(\boldsymbol{r}_2 - \boldsymbol{r}_2')\, 1/r_{12} , \tag{2.4}$$

where

$$r_{12} = | \boldsymbol{r}_1 - \boldsymbol{r}_2 | .$$

Let us denote the Hartree-Fock (HF) orbitals by $\varphi_1 \ldots \varphi_N$. The equations of the HF approximation are as follows. The HF energy is

$$E_F = \sum_{i=1}^{N} \langle \varphi_i | t + \tfrac{1}{2} U | \varphi_i \rangle , \tag{2.5}$$

where

$$U = \sum_{S=1}^{N} U_s \tag{2.6}$$

and

$$U_s = \langle 1 | U_s | 1' \rangle = \int \varphi_s^*(2) \left[\langle 12 | v | 1'2' \rangle - \langle 12 | v | 2'1' \rangle \right] \cdot \varphi_s(2')\, dq_2\, dq_2' . \tag{2.7}$$

(q = spatial and spin coordinates.) U_s is the HF potential (including exchange) associated with the orbital φ_s. Using (2.4) we see that, if we operate with U_s on an arbitrary function we get the conventional HF Coulomb and Exchange potentials:

$$\begin{aligned} U_s(1) f(1) &= \int \langle 1 | U_s | 1' \rangle f(1')\, dq_1' \\ &= \int \varphi_s^*(2) [\delta(1-1')\, \delta(2-2') \\ &\quad - \delta(1-2')\, \delta(2-1')]\, \frac{1}{r_{12}}\, \varphi_s(2') f(1')\, dq_2\, dq_2'\, dq_1' \\ &= \int \frac{|\varphi_s(2)|^2}{r_{12}}\, dq_2 f(1) - \int \frac{\varphi_s(1)\, \varphi_s^*(2) f(2)}{r_{12}}\, dq_2 . \end{aligned} \tag{2.8}$$

The HF equations are

$$H_F \varphi_i = \varepsilon_i \varphi_i , \quad (i = 1, \ldots, N) , \tag{2.9}$$

where

$$H_F = t + U , \tag{2.10}$$

and for the total energy we get

$$E_F = \sum_{i=1}^{N} \varepsilon_i - \tfrac{1}{2} \sum_{i,j=1}^{N} \varepsilon_{ij} , \tag{2.11}$$

where

$$\varepsilon_{ij} = \langle \varphi_i | U_j | \varphi_i \rangle = \langle \varphi_j | U_i | \varphi_j \rangle . \tag{2.12}$$

III. The Equation for the Exact Orthogonalized Wave Function of the Valence Electrons

Let us devide now the electrons of the system into K core electrons and $n = N - K$ valence electrons, where n is arbitrarily large. We assume that the K core electrons are in closed shells. The valence electrons are generally in open shells although in order to keep the formalism reasonably simple in the first presentation we shall treat the valence electrons as if they would also be in closed shells. The generalization to open shells, although not trivial, will be straightforward.

We represent the system by the wave function

$$\Psi_T = (N!)^{-1/2} \tilde{A} \{ \varphi_1(1) \ldots \varphi_K(K)\, \Psi(K+1 \ldots N) \} , \tag{3.1}$$

where the core electrons are represented by the spin-orbitals $\varphi_1 \ldots \varphi_K$ and the valence electrons by the antisymmetric correlated wave function $\Psi(1, 2, \ldots, n)$. [$(N)^{-1/2}$ is the same normalization factor as in the HF determinant and $\tilde{A}$ is an antisymmetrizer operator.]

After the core-valence separation has been made the correlation effects are of three kind: There is

A) valence-valence correlation;

B) valence-core correlation;

C) core-core correlation.

In (3.1) the first is fully taken into account the second and the third neglected. The choice of (3.1) is motivated by the experience gained in previous pseudopotential studies [15] which have shown that the valence-valence correlation effects are crucial for accurate calculations; therefore this effect must be built into the theory exactly. The omission of the second and third correlation effects is motivated by the desire of not making the formalism too complicated and by the assumption that these effects being less important than the valence-valence correlation can be later incorporated into the theory as refinements.

We derive now the exact equation for the valence electron wave function Ψ. An "exact" equation is defined as follows. We take the wave function (3.1) and form the average value of the Hamiltonian (2.1). We vary the average value with respect to Ψ taking into account the subsidiary conditions. The resulting equation, yielding the best Ψ (for a given set of core orbitals) is defined as the exact equation for Ψ.

The matrix component of the Hamiltonian with respect to a function of the type (3.1) has been derived before, in the theory of correlated wave functions for atoms [17] and also for Fermion systems [18] with general, non-local interactions v_{ij}. Inspection of the derivation shows that the formula previously derived is valid for the atomic-molecular Hamiltonian (2.1) with a slight change in the notation. We get, using Eq. (4.6) of the Ref. [17]:

$$\begin{aligned}\langle \Psi_{\mathrm{T}} | H | \Psi_{\mathrm{T}} \rangle &= \frac{1}{(n-1)!} \langle \Psi | t_1 + \sum_{S=1}^{K} U_s(1) | \Psi \rangle \\ &+ \frac{1}{2(n-2)!} \langle \Psi | v_{12} | \Psi \rangle \\ &+ \frac{1}{n!} \left\{ \sum_{S=1}^{K} \langle \varphi_s | t | \varphi_s \rangle + \tfrac{1}{2} \sum_{s,t=1}^{K} \varepsilon_{st} \right\}, \qquad (3.2)\end{aligned}$$

and [Eq. (4.7) of Ref. [17]]

$$\langle \Psi_{\mathrm{T}} | \Psi_{\mathrm{T}} \rangle = \frac{1}{n!}. \qquad (3.3)$$

In the derivation of (3.2) and (3.3) it is assumed that the one-electron orbitals are orthonormal,

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}, \qquad (3.4)$$

and the valence electron function is strong-orthogonal to the one-electron orbitals:

$$\int \Psi(1, 2, \ldots, n) \varphi_s^*(1) \, \mathrm{d}q_1 \equiv 0, \quad (s = 1, \ldots, K), \qquad (3.5)$$

and it is normalized

$$\langle \Psi | \Psi \rangle = 1. \qquad (3.6)$$

It had been shown [17] that the strong-orthogonality condition does not restrict the generality of (3.1). By this statement we mean the following. Let Ψ_0 be an arbitrary function not satisfying (3.5). Let P be the operator

$$P = P_1 P_2 \ldots P_n, \qquad (3.7)$$

where

$$P_1 f(1) = f(1) - \sum_{S=1}^{K} \varphi_s(1) \int \varphi_s^*(2) f(2) \, \mathrm{d}q_2. \qquad (3.8)$$

It is easy to see that

$$\Psi = P \Psi_0 \qquad (3.9)$$

will satisfy (3.5) regardless of the form of Ψ_0. The statement about the generality of (3.1) means that

$$\begin{aligned}&\tilde{A} \{ \varphi_1(1) \ldots \varphi_K(K) \Psi_0 (K+1, \ldots, N) \} \\ &= \tilde{A} \{ \varphi_1(1) \ldots \varphi_K(K) P \Psi_0 (K+1, \ldots, N) \} \\ &= \tilde{A} \{ \varphi_1(1) \ldots \varphi_K(K) \Psi (K+1, \ldots, N) \}, \qquad (3.10)\end{aligned}$$

meaning that the total wave function does not change when an arbitrary Ψ_0 is replaced by the strong-orthogonal $P \Psi_0$.

Using (3.2) (3.3) and taking into account the antisymmetric character of Ψ we obtain

$$E_{\mathrm{av.}} = \frac{\langle \Psi_{\mathrm{T}} | H | \Psi_{\mathrm{T}} \rangle}{\langle \Psi_{\mathrm{T}} | \Psi_{\mathrm{T}} \rangle} = \langle \Psi | H(n) | \Psi \rangle + E_{\mathrm{F}}(K), \qquad (3.11)$$

where

$$H(n) = \sum_{i=1}^{n} \left(t_i + \sum_{S=1}^{K} U_s(i) \right) + \tfrac{1}{2} \sum_{i,j=1}^{n} v_{ij}, \qquad (3.12)$$

and

$$E_{\mathrm{F}}(K) = \sum_{S=1}^{K} \langle \varphi_s | t | \varphi_s \rangle + \tfrac{1}{2} \sum_{s,t=1}^{K} \varepsilon_{st}. \qquad (3.13)$$

In (3.11) the first term is the energy of the valence electrons (including core-valence interactions) and the second is the HF energy of the core electrons.

We will now vary $E_{\mathrm{av.}}$ with respect to Ψ[19]. The subsidiary conditions are (3.5) and (3.6). The condition (3.5) must be changed into integral conditions. This can be done [19] by expanding the integral in terms of the solutions of (2.9) which form a complete system:

$$\int \Psi(1,2,\dots,n)\,\varphi_s^*(1)\,dq_1 = \sum_{\alpha,\beta,\dots,\omega=1}^{\infty} C_s(\alpha,\beta,\dots,\omega)\,\varphi_\alpha(2)\,\varphi_\beta(3)\dots\varphi_\omega(n)\,. \tag{3.14}$$

Condition (3.5) now becomes

$$C_s(\alpha,\beta,\dots,\omega)=0\,,$$
$$\{s=1,\dots,K;\ \alpha,\beta,\dots,\omega=1,2,\dots,\infty\}\,, \tag{3.15}$$

where

$$C_s(\alpha,\beta,\dots,\omega)=\int \Psi(1,2,\dots,n)\cdot\varphi_s^*(1)\,\varphi_\alpha^*(2)\,\varphi_\beta^*(3)\dots\varphi_\omega^*(n)\,dq\,, \tag{3.16}$$

and dq means integration over all coordinates. Introducing the Lagrangian multipliers $-\lambda(s,\alpha,\beta,\dots,\omega)$ for (3.15) and $-E$ for (3.6) we obtain the variational equation in the form

$$\delta\Big\{\langle\Psi|H(n)|\Psi\rangle + E_{\mathrm{F}}(K) - E\langle\Psi|\Psi\rangle - \sum_{S=1}^{K}\ \sum_{\alpha,\beta,\dots,\omega=1}^{\infty}\lambda(s,\alpha,\beta,\dots,\omega)\times\langle\Psi|\varphi_s\varphi_\alpha\varphi_\beta\dots\varphi_\omega\rangle\Big\}=0\,. \tag{3.17}$$

Carrying out the variation we obtain

$$H(n)\,\Psi=E\,\Psi + \sum_{S=1}^{K}\ \sum_{\alpha\dots\omega=1}^{\infty}\lambda(s,\alpha\dots\omega)\,\varphi_s(1)\,\varphi_\alpha(2)\dots\varphi_\omega(n)\,. \tag{3.18}$$

Let us write the operator P_1 introduced in (3.8) in the form

$$P_1=1-\Omega_1\,, \tag{3.19}$$

where

$$\Omega_1 f(1)=\sum_{S=1}^{K}\varphi_s(1)\int\varphi_s^*(2)\,f(2)\,dq_2\,. \tag{3.20}$$

Using (3.7) we can write

$$P=P_1\dots P_n=(1-\Omega_1)(1-\Omega_2)\dots(1-\Omega_n)\,, \tag{3.21}$$

and combining the Ω's into one term we can write

$$P=1-\Omega\,. \tag{3.22}$$

Since these operators play an important role in our discussions we summarize here their properties. First

$$P_1\varphi_j(1)=0 \quad \text{if } j=1,2,\dots,K\,; \tag{3.23}$$
$$P_1\varphi_j(1)=\varphi_j(1) \quad \text{if } j=K+1,K+2,\dots,\infty\,.$$

If $f(1,2,\dots,n)$ is an n-particle function which satisfies the strong orthogonality condition (3.5) then

$$P f=f\,. \tag{3.24}$$

It is easy to see that if the orbitals in (3.20) are the solutions of the HF equations (2.9) then

$$P H_{\mathrm{F}}=H_{\mathrm{F}}P\,. \tag{3.25}$$

Finally P is a projection operator therefore

$$P^2=P\,. \tag{3.26}$$

In order to eliminate the λ's from (3.18) operate on this equation from the left by P:

$$P\,H(n)\,\Psi=E\,\Psi\,. \tag{3.27}$$

Taking into account the form of $H(n)$, Eq. (3.12), we can write (3.27) in the form

$$\Big\{\sum_{i=1}^{n}H_{\mathrm{F}}(i)+P\,Q\Big\}\,\Psi=E\,\Psi\,, \tag{3.28}$$

where

$$Q\equiv\tfrac{1}{2}\sum_{i,j=1}^{n}v_{ij}-\sum_{i=1}^{n}\ \sum_{S=K+1}^{N}U_s(i)\,. \tag{3.29}$$

Equation (3.28) is the exact equation for Ψ.

We shall consider Eq. (3.28) to be the basic equation for the valence electron wave function of those atoms and molecules to which our theory can be applied. Here we summarize the properties of this equation.

First it is clear that the operator in (3.28) is not Hermitian since P und Q are not commuting. Despite of this we shall show that the variation principle can be applied to the calculation of approximate solutions of (3.28). Here we note that a special case of Eq. (3.28), an equation for the two valence electrons of an atom, was derived some years ago by the author (Reference [19]). In connection with the two-electron equation of Ref. [19], Huzinaga and Cantu stated [20] that, since the equation is not Hermitian, the variation principle cannot be used to obtain approximate solutions. The derivation presented below will show that the statement by Huzinaga and Cantu [20] was erroneous.

Let

$$H_0\equiv\sum_{i=1}^{n}H_{\mathrm{F}}(i) \tag{3.29 a}$$

and

$$\hat{H}\equiv H_0+P\,Q\,. \tag{3.30}$$

First we show now that $\hat{H}$ is Hermitian with respect to strong-orthogonal functions i.e. with respect to functions which satisfy (3.24). Let f and g be arbitrary n-electron functions which both satisfy (3.24). Then

$$\begin{aligned}\langle f|PQ|g\rangle &= \langle Pf|Q|g\rangle = \langle f|Q|g\rangle \\ &= \langle g|Q|f\rangle^* = \langle Pg|Q|f\rangle^* = \langle g|PQ|f\rangle^*,\end{aligned} \tag{3.31}$$

where we took into account that Q is Hermitian. Equation (3.31) shows that PQ is Hermitian with respect to strong orthogonal functions and since H_0 is Hermitian, the theorem is proved.

In order to construct approximate solutions of (3.28) with the variation method we use a modified form of a derivation presented by Merzbacher[21]. Let Ψ be an n-electron trial function satisfying (3.24). Consider the quantity

$$\lambda[\Psi] \equiv \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{3.32}$$

Since $\hat{H}$ is "strong-orthogonal-Hermitian" λ will be real. Let us assume that λ has a lower bound which is obtained for a certain strong-orthogonal wave function Ψ_0, i. e.

$$\lambda_0 = \lambda[\Psi_0] \leqq \lambda \tag{3.33}$$

for all λ's. Now put

$$\Psi = \Psi_0 + \varepsilon\,\Phi, \tag{3.34}$$

where Φ is strong-orthogonal and ε is a small positive number. Using (3.33) we obtain

$$\lambda_0 \leqq \lambda[\Psi_0 + \varepsilon\,\Phi]. \tag{3.35}$$

Using (3.32) and (3.35) we get

$$\begin{aligned}&\pm\varepsilon\{\langle\Phi|\hat{H}-\lambda_0|\Psi_0\rangle \\ &\quad + \langle\Psi_0|\hat{H}-\lambda_0|\Phi\rangle \pm \varepsilon\langle\Phi|\hat{H}-\lambda_0|\Phi\rangle\} \geqq 0.\end{aligned} \tag{3.36}$$

Since Φ is strong-orthogonal and λ_0 is the lower bound we get that

$$S \equiv \langle\Phi|\hat{H}-\lambda_0|\Phi\rangle \geqq 0, \tag{3.37}$$

and using this equation we obtain from (3.36)

$$-\varepsilon S \leqq \langle\Phi|\hat{H}-\lambda_0|\Psi_0\rangle + \langle\Psi_0|\hat{H}-\lambda_0|\Phi\rangle \leqq +\varepsilon S \tag{3.38}$$

and if $\varepsilon \to 0$

$$\langle\Phi|\hat{H}-\lambda_0|\Psi_0\rangle + \langle\Phi|\hat{H}-\lambda_0|\Psi_0\rangle^* = 0, \tag{3.39}$$

where we took into account that $\hat{H}$ is strong-orthogonal-Hermitian. Now let

$$\Phi = (\hat{H}-\lambda_0)\,\Psi_0. \tag{3.40}$$

This function must be strong-orthogonal. Taking into account that Ψ_0 is strong-orthogonal and taking into account (3.25) and (3.26) we obtain

$$P\Phi = P(\hat{H}-\lambda_0)\,\Psi_0 = (\hat{H}-\lambda_0)\,\Psi_0 = \Phi, \tag{3.41}$$

which shows that (3.40) is strong-orthogonal. Substituting (3.40) into (3.39) we get

$$\langle(\hat{H}-\lambda_0)\,\Psi_0|(\hat{H}-\lambda_0)\,\Psi_0\rangle = 0, \tag{3.42}$$

from which it follows that

$$(\hat{H}-\lambda_0)\,\Psi_0 = 0. \tag{3.43}$$

This equation means that the wave function Ψ_0 which minimizes (3.32) is the exact solution of Eq. (3.28) and λ_0 will be, by definition, the lowest eigenvalue of (3.28). λ_0 corresponds to the ground state of the valence electrons. Solutions for the excited states (for a fixed $\hat{H}$) can be constructed similarly[21]. It is clear from the derivation that the solutions constructed this way will be strong-orthogonal to the core orbitals. It is easy to show that if Ψ_i and Ψ_j are strong-orthogonal solutions of (3.28) for different eigenvalues then

$$\langle\Psi_i|\Psi_j\rangle = 0. \tag{3.44}$$

It is proved now that the variation method can be applied to the calculation of approximate solutions of Equation (3.28). In the case of the ground state, for any strong-orthogonal trial function ψ, we get, according to (3.33)

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geqq E_0 \tag{3.45}$$

where E_0 is the eigenvalue for the ground state.

We note that the energy expression used in the theory of correlated wave functions[22] is a special case of the expression (3.32); in that theory Ψ is a correlated 2-electron function. In that case calculations have shown[23] that the variation method can be used for the calculation of approximate energy values.

IV. The Exact Equation for the Pseudowavefunction of the Valence Electrons

Having obtained the equation for the exact orthogonalized valence electron wave function, Eq. (3.28), we shall introduce now the equation for the exact valence electron pseudowavefunction. Let Ψ be the exact pseudowavefunction for the n valence electrons. It is defined by the equation

$$\hat{\Psi} = P\,\Psi\,, \tag{4.1}$$

where $\hat{\Psi}$ is the exact solution of (3.28). (From here on the orthogonalized functions will be indicated by caret.) Let

$$V(i) = \sum_{S=1}^{K} \langle i \,|\, \varphi_s \rangle \langle F_s | \tag{4.2}$$

be a general, one-electron pseudopotential operator[9] where F_s is an arbitrary function possesing the symmetry of the atom or molecule and let

$$V_0 \equiv \sum_{i=1}^{n} V(i)\,. \tag{4.3}$$

We state that the exact pseudopotential equation, corresponding to Eq. (3.28), is as follows:

$$H_{\text{P}}\,\Psi = E\,\Psi\,, \tag{4.4}$$

with

$$H_{\text{P}} \equiv H_0 + V_0 + Q\,P\,, \tag{4.5}$$

where the four operators are defined by (3.29 a), (4.3), (3.29) and (3.7).

In order to show that (4.4) is equivalent to (3.28) let us assume that (4.4) has solutions for which $P\,\Psi \neq 0$. Let Ψ be such a solution. Multiplying (4.4) from the left by P we get

$$P(H_0 + V_0 + Q\,P)\,\Psi = E\,P\,\Psi\,. \tag{4.6}$$

Since P commutes with H_0 and since

$$P\,V_0 = 0 \tag{4.7}$$

we obtain

$$(H_0 + P\,Q)\,(P\,\Psi) = E(P\,\Psi)\,, \tag{4.8}$$

or, using the notation (3.30) and denoting $P\,\Psi$ by $\hat{\Psi}$ we get

$$\hat{H}\,\hat{\Psi} = E\,\hat{\Psi}\,. \tag{4.9}$$

We see that $\hat{\Psi}$ is a solution of (3.28) with the eigenvalue E. This means that if Ψ is a pseudowavefunction which is the solution of (4.4) with the eigenvalue E then the orthogonalized function which is related to Ψ by Eq. (4.1) will be the solution of (3.28) with the same eigenvalue. Therefore those eigenfunctions of (4.4) for which $P\Psi \neq 0$, will belong to eigenvalues which are equal to the corresponding eigenvalues of (3.28). It is clear that this argument can be applied to non-degenerate as well as to degenerate states.

The structure of Eq. (4.4) is such that it will have solutions for which $P\,\Psi = 0$. From (3.22) we see that $P = 1 - \Omega$, where Ω is a projection operator onto the core states. The functions therefore which satisfy the $P\,\Psi = 0$ condition are antisymmetrized products of an arbitrary selection of core orbitals. Let $\varphi_\alpha, \varphi_\beta \ldots, \varphi_\omega$ be a selection of n core orbitals and let

$$\psi_{\text{C}} \equiv \det\,[\varphi_\alpha\,\varphi_\beta \ldots \varphi_\omega]\,. \tag{4.10}$$

We have

$$P\,\psi_{\text{C}} = 0\,. \tag{4.11}$$

For the one-electron pseudopotentials we put[5, 6]

$$\langle F_{\text{s}} | = (\varepsilon_{\text{V}} - \varepsilon_{\text{s}})\,\langle \varphi_{\text{s}} |\,, \tag{4.12}$$

where φ_{s} is a HF core orbital, ε_{s} is the corresponding eigenvalue and ε_{V} is any one of the valence level HF eigenvalues. Substituting (4.12) into (4.4) and taking into account that

$$H_0\,\psi_{\text{C}} = (\varepsilon_\alpha + \varepsilon_\beta + \ldots + \varepsilon_\omega)\,\psi_{\text{C}}\,, \tag{4.13}$$

$$V_0\,\psi_{\text{C}} = n\,\varepsilon_{\text{V}} - (\varepsilon_\alpha + \varepsilon_\beta + \ldots\; + \varepsilon_\omega)\,\psi_{\text{C}}\,, \tag{4.14}$$

we obtain that ψ_{C} is a solution of (4.4) with

$$E = n\,\varepsilon_{\text{V}}\,. \tag{4.15}$$

We shall call the solutions for which $P\,\psi \neq 0$ "valence" solutions and those for which $P\,\psi = 0$ "core" solutions. We shall show that the latter can be eliminated at each step of the development of the theory.

We have therefore two equivalent equations from which we can determine the wave function of the valence electrons. Equation (3.28) determines those wave functions which are strong-orthogonal to the core orbitals; Eq. (4.4) determines the pseudowavefunctions which do not have to satisfy the orthogonality conditions. The presence of the pseudopotentials (4.2) prevents the valence electrons from "falling" into the core.

Reviewing further the properties of Eq. (4.4) we observe that H_{P} is not Hermitian. It is easy to show however that the eigenvalues of (4.4) belonging to valence solutions will be real. Let us write down (4.4) and the complex conjugate equation:

$$H_{\text{P}}\,\Psi = E\,\Psi\,, \tag{4.16}$$

$$H_{\text{P}}{}^*\,\Psi^* = E^*\,\Psi^*\,. \tag{4.17}$$

Multiplying the first equation from the left by $(P\,\Psi)^*$ the second by $(P\,\Psi)$, integrating and substracting the second from the first we obtain easily that

$$E^* = E . \tag{4.18}$$

This result, of course, follows also from the fact that the valence eigenvalues of (4.4) are equal to the "strong-orthogonal" eigenvalues of (3.28) which are real.

Since H_P is not Hermitian – not even with respect to a certain class of functions – the variation method cannot be used for the calculation of approximate solutions. It was pointed out however by Merzbacher[24] that representation theory can be used for proving the existence of solutions of the eigenvalue equation of non-Hermitian operators and for the calculation of approximate solutions. Here we present Merzbacher's argument[24] modified in such a way as to exclude the core solutions. Let us expand the eigenfunctions of (4.4) in terms of a complete set of n-electron functions:

$$\Psi = \sum_{i=1}^{\infty} C_i \Psi_i . \tag{4.19}$$

These functions are arbitrary except for the single restriction that

$$P \Psi_i \neq 0 . \tag{4.20}$$

Substituting (4.19) into (4.4) we get the equation

$$\sum_{i=1}^{\infty} (H_{ji} - E S_{ji}) C_i = 0 , \tag{4.21}$$

where

$$H_{ji} = \langle \Psi_j | H_P | \Psi_i \rangle , \tag{4.22}$$

$$S_{ji} = \langle \Psi_j | \Psi_i \rangle . \tag{4.23}$$

(4.21) will have solutions if

$$\det [H_{ji} - E S_{ji}] = 0 , \quad (j, i = 1, 2, \dots, \infty) , \tag{4.24}$$

which is the usual secular equation, but of course, the approximate energy computed from (4.24) for a finite set of trial functions, will not be an upper limit to the exact energy. Condition (4.20) will insure that the energy values computed from (4.24) will converge toward the valence eigenvalues of (4.4). Although the approximate energies will not be upper limits the presence of the pseudopotentials (4.2) will prevent the energy from converging toward the core energies[25].

As we mentioned above Weeks and Rice developed a pseudopotential formalism applicable to atoms with more than one valence electrons[13]. Their method consisted of substituting $P\Psi$ into the energy expression (3.11) and varying the total energy of the system with respect to the pseudowavefunction. It is easy to see that this method leads to an equation which can be obtained from (4.4) by multiplying (4.4) from the left by P and leaving the equation in terms of pseudowavefunctions. We obtain this way the equation

$$[H_0 + P Q P + (E - H_0) \Omega] \Psi = E \Psi , \tag{4.25}$$

where we have used (3.22), (3.25) and (4.7). This equation, in the same way as (4.4), is equivalent to (3.28).

The comparison between (4.4) and (4.25) is favorable to the former. Although the operator in (4.25) is Hermitian and H_P is not, H_P has two crucial advantages. Unlike the operator of (4.25), H_P does not depend on E and it has a much simpler structure. Both of these features are advantages if we want to use the equations directly in calculations. The absence of E and, even more importantly, the simplicity of H_P will be crucial advantages when we derive a simple model Hamiltonian[26] from the exact equation. As we will show below the transition from Eq. (4.4) to a simple model Hamiltonian will be straightforward; a similar transition, from (4.25) would not be nearly as simple.

Summarizing the contents of this Section, we have found an equation for the n-electron pseudowavefunction which is of surprisingly simple structure and exact in the sense of giving the minimum energy. The equation is valid for any atom or molecule. The Hamiltonian H_P does not depend on Ψ and/or on E. Although H_P is not Hermitian, the valence eigenvalues are real and the existence of exact solutions can be demonstrated and approximate solutions can be constructed by expanding Ψ in terms of a complete set subjected only to the condition (4.20) excluding the core orbitals from the expansion.

After the presentation of Eq. (3.28) we identified that equation as the basic equation for the valence electrons. Now we see that Eq. (4.4) yields the same eigenvalues as Eq. (3.28) and the eigenfunctions of (3.28) are given as the eigenfunctions of (4.4) multiplied by P. The pseudopotential equation therefore can also be identified as the basic equation for the valence electrons. The existence of an exact many-electron pseudopotential equation is not surprising if we recall that, although in the total wave function of the system, Eq. (3.1), we have assumed Ψ to be strong orthogonal to the core orbitals, the principles of Quantum Mechanics do not prescribe such an orthogonalization. Instead of orthogonalizing Ψ as we have done in Sect. III, we could have left Ψ non-orthogonal – a pseudowavefunction – and could have looked for the equation determining the best such function, without going through the process of deriving first Eq. (3.28) for the orthogonalized wave function. The pseudopotential equation (4.4) determines the valence electron properties just as exactly and fully as the more conventional Equation (3.28). *The introduction of a many-electron pseudowavefunction i. e. a wave function which is not orthogonal to the core orbitals does not a priori imply the introduction of an approximation.*

Although Eq. (4.4) is equivalent to (3.28) we shall consider the pseudopotential equation more as a conceptual rather than a computational basis for the pseudopotential theory. The main reason for this is the absence of Hermitian property in H_{P}; the variation method cannot be applied. In the next Section we shall show that a simple model Hamiltonian can easily be derived from (4.4). We shall consider Eq. (4.4) not as a starting point of actual calculations (although such calculations can be made using the expansion method presented above) but as an exact equation from which new, simple model Hamiltonians can be derived and which can be used to test the accuracy of already existing pseudopotential models.

V. Model Hamiltonians

In almost all pseudopotential studies [15] the valence electrons are represented by a model Hamiltonian which has the following form:

$$H_{\mathrm{M}}=\sum_{i=1}^{n} H_{\mathrm{m}}(i)+\tfrac{1}{2}\sum_{i,j=1}^{n}(1/r_{ij}), \tag{5.1}$$

where H_{m} is a one-electron operator representing core-valence interactions and including the pseudopotentials and the second term is the valence-valence interaction.

Let us rewrite Eq. (4.4) as follows:

$$\{H_0+V_0+Q+Q(P-1)\}\,\Psi=E\,\Psi. \tag{5.2}$$

We obtain (5.1) from (5.2) by two approximations: first we omit the last term on the feft side of (5.2). This step will be called the $P\rightarrow 1$ ("P replaced by 1") approximation since it amounts to replacing P by the unity operator in Equation (4.4). We obtain this way

$$\{H_0+V_0+Q\}\,\Psi=E\,\Psi. \tag{5.3}$$

Taking into account the form of these operators, Eqs. (3.29), (3.29 a) and (4.3) and replacing the operator symbol v_{ij} in Q by $1/r_{ij}$ we obtain that

$$H_0+V_0+Q=S+T, \tag{5.4}$$

where

$$S\equiv\sum_{i=1}^{n}\{H_{\mathrm{c}}(i)+V(i)\}, \tag{5.5}$$

and

$$T\equiv\frac{1}{2}\sum_{i,j=1}^{n}\frac{1}{r_{ij}}. \tag{5.6}$$

In (5.5) the operator H_{c} is the HF operator representing the core:

$$H_{\mathrm{c}}\equiv t+\sum_{S=1}^{K}U_s. \tag{5.7}$$

The second approximation is to replace $H_{\mathrm{c}}+V$ by the model operator H_{m}:

$$H_{\mathrm{c}}+V\rightarrow H_{\mathrm{m}}. \tag{5.8}$$

Making this substitution in (5.5) we get

$$S=\sum_{i=1}^{n}H_{\mathrm{m}}(i), \tag{5.9}$$

and using (5.9), (5.6) and (5.4) the Eq. (5.3) becomes

$$(S+T)\,\Psi=\left\{\sum_i H_{\mathrm{m}}(i)+\frac{1}{2}\sum_{i,j}\frac{1}{r_{ij}}\right\}\Psi=E\,\Psi, \tag{5.10}$$

which is identical with (5.1).

We clarified therefore that the videly used model Hamiltonian (5.1) is removed from the exact H_{P} by just two approximations, by the $P\rightarrow 1$, which amounts to omitting $Q(P-1)$ and by the replacement of the core-valence interaction operator $H_{\mathrm{c}}+V$ by the model operator H_{m}. The second of these is a one-electron approximation which has been discussed extensively [15]. Since in this paper we concentrate on the many-electron effects we shall discuss the $P\rightarrow 1$ approximation in detail and omit a discussion of the construction of H_{m}.

The $P\rightarrow 1$ approximation can be motivated by at least three arguments. First, with the removal of P we gotten rid of the core solutions of (4.4), discussed above. Secondly, the omission of P means the removal of the non-Hermitian part of H_{P} (assuming that the pseudopotentials V are Hermitian).

Thirdly, the product QP is responsible for the greatest mathematical difficulties. For example, in the case of an atom with two valence electrons[27], if the pseudowavefunction contains the interelectronic coordinate r_{12}, matrix components involving QP will generate integrals containing the product $(r_{12}r_{13}r_{23})$ which can be computed only very laboriously[28]. If $Q(P-1)$ is omitted only simple integrals with r_{12} will occur[27].

In order to justify the $P \rightarrow 1$ approximation we note that the operator in (5.3) which is obtained after the $P \rightarrow 1$ is carried out, is very plausible physically. From (5.5) and (5.6) we see that this operator contains the HF core-valence interaction operator H_c plus the pseudopotentials V which keep the valence electrons out of the core, and of course, the valence-valence interaction potential T. In addition to this argument we shall show below for the case of atoms with two valence electrons that viewing the omitted operator $Q(P-1)$ as a "perturbation" it is easy to demonstrate that the first order perturbation energy resulting from this operator is negligibly small. We expect that it will be possible to extrapolate this argument to other, more complicated systems to which the pseudopotential theory can be applied.

VI. Example: Atoms with Two Valence Electrons

For an atom with two valence electrons the exact pseudopotential equation reads as follows:

$$\{H_F(1)+H_F(2)+V(1)+V(2)+Q_{12}P_{12}\}\Psi=E\Psi, \quad (6.1)$$

with

$$Q_{12}\equiv\frac{1}{r_{12}}-U_\alpha(1)-U_\alpha(2)-U_\beta(1)-U_\beta(2) \quad (6.2)$$

and

$$P_{12}=P_1P_2. \quad (6.3)$$

U_α and U_β are the HF potentials for the two valence states.

The model equation, Eq. (5.1) will be for this case

$$\left(H_m(1)+H_m(2)+\frac{1}{r_{12}}\right)\Psi=E\Psi. \quad (6.4)$$

As outlined above, we arrive at (6.4) by rewriting first (6.1) as follows:

$$\{H_F(1)+H_F(2)+V(1)+V(2)+Q_{12}+V_P\}\cdot\Psi=E\Psi, \quad (6.5)$$

where V_P is the "perturbation":

$$V_P\equiv Q_{12}(P_{12}-1). \quad (6.6)$$

Taking into account (6.2) we get

$$\left\{H_c(1)+H_c(2)+V(1)+V(2)+\frac{1}{r_{12}}+V_P\right\}\Psi=E\Psi. \quad (6.7)$$

Now let us assume that H_c+V can accurately be replaced by a mathematically simple model operator H_m. Introducing this operator into (6.7) we get

$$\left\{H_m(1)+H_m(2)+\frac{1}{r_{12}}+V_P\right\}\Psi=E\Psi \quad (6.8)$$

and we obtain (6.4) by omitting V_P from this equation.

Let us assume that we want to compute approximate solutions of (6.8) by using perturbation theory. The "unperturbed" equation is (6.4). Let us consider a non-degenerate state and let Ψ and E be the solutions of (6.4) and $\tilde{E}$ be the eigenvalue of (6.8) for this state. Then, in the first order of the perturbation theory we obtain

$$\tilde{E}=E+\int\Psi^* V_P\Psi\,dq, \quad (6.9)$$

where we have tacitly assumed that H_m is Hermitian, so that a perturbation expansion can be built on the solutions of (6.4).

Our goal is to show that the integral in (6.9) is negligibly small. For an accurate qualitative argument let us replace the (correlated) wave function Ψ by the product $\varphi_0(1)\varphi_0(2)$ where φ_0 is a pseudowavefunction for the valence state. A logical choice for φ_0 is the solution of the equation

$$(H_F+V)\varphi_0=\varepsilon_0\varphi_0. \quad (6.10)$$

By choosing φ_0 to be the eigenfunction of H_F+V rather than of H_c+V we are taking into account the valence-valence interaction in the HF approximation. We obtain

$$E_P\equiv\int\Psi^* V_P\Psi\,dq$$
$$=\int\varphi_0^*(1)\varphi_0^*(2)Q_{12}\hat{\varphi}_0(1)\hat{\varphi}_0(2)\,dq_{12}$$
$$-\int\varphi_0^*(1)\varphi_0^*(2)Q_{12}\varphi_0(1)\varphi_0(2)\,dq_{12}, \quad (6.11)$$

where

$$\hat{\varphi}_0(1)=P_1\varphi_0(1). \quad (6.12)$$

Let R_0 and $\hat{R}_0$ be the radial parts of φ_0 and $\hat{\varphi}_0$, and let

$$P_0=rR_0, \quad \hat{P}_0=r\hat{R}_0. \quad (6.13)$$

Denoting by $E_P{}^1$ that part of E_P which comes from $1/r_{12}$ we obtain

$$E_P{}^1 = \sum_{j=1}^{\infty} a_j [\hat{F}_j - F_j] \,, \tag{6.14}$$

where the a_j are coefficients resulting from the angular integration and

$$\hat{F}_j \equiv \int \hat{P}_0(r_1) P_0(r_1) \hat{P}_0(r_2) P_0(r_2) L_j(r_1 r_2) \, dr_1 \, dr_2 \,, \tag{6.15}$$

$$F_j \equiv \int P_0{}^2(r_1) P_0{}^2(r_2) \, L_j(r_1 r_2) \, dr_1 \, dr_2 \,, \tag{6.16}$$

$$L_j \equiv r_<^j / r_>^{j+1} \,. \tag{6.17}$$

It is known from previous studies[8, 9] that the solutions of (6.10) are of the form

$$\varphi_0 = \varphi_V + \sum_{S=1}^{K} a_s \varphi_s \tag{6.18}$$

where φ_V and φ_s are valence and core HF orbitals and

$$a_s = \langle \varphi_0 | \varphi_s \rangle \,. \tag{6.19}$$

For $\hat{\varphi}_0$ we get

$$\hat{\varphi}_0 = \varphi_V \,. \tag{6.20}$$

Similarly we obtain

$$P_0 = P_V + \sum_{S=1}^{K} a_s P_s \,, \tag{6.21}$$

and

$$\hat{P}_0 = P_V \,. \tag{6.22}$$

We state that in good approximation

$$P_0 \hat{P}_0 \approx P_0{}^2 \,. \tag{6.23}$$

This approximation can be established by analyzing (6.21) and (6.22). In the valence region where the bulk of both functions is located $P_0 = \hat{P}_0$ exactly. Since $\hat{P}_0$ is a HF function and P_0 is a pseudowavefunction, in the core region $\hat{P}_0$ will have oscillations while P_0 is a smooth function. Both will be small in the core region (because of $P = rR$) and for any reasonable set of a's which should be small for a reasonable pseudopotential[29], the $P_0{}^2$ will be an average of $\hat{P}_0{}^2$.

Therefore the approximation (6.23) is exact in the valence region and qualitatively accurate in the core region.

Using (6.23) we get

$$\hat{F}_j \approx F_j \tag{6.24}$$

and

$$E_P{}^1 \approx 0 \,. \tag{6.25}$$

It is easy to show that similar arguments can be constructed for that part of E_P which comes from U_α and U_β. We may write therefore that in good approximation

$$E_P \approx 0 \,, \tag{6.26}$$

and using this result in (6.9) we obtain

$$\tilde{E} \approx E \,. \tag{6.27}$$

We conclude that Eq. (6.8) can be replaced by Eq. (6.4) in a good approximation, i.e. the model equation (6.4) will be a good approximation of the exact equation (6.1) if the one-electron model operators H_m are accurate replacements for the operators $H_c + V$.

Here we note that Eq. (6.4) has been used by Hellmann[3], Szasz and McGinn[30], Schwarz[31] and Bardsley[32] for the calculation of energy levels of atoms with two valence electrons. Using Hellmann type model potentials[3] for H_m, Schwarz and Bardsley obtained highly accurate results. In the light of the preceding discussion we may say that these accurate results were not fortuitous but can be explained by the fact that the model equation is removed from the exact equation by just two plausible approximations. Looking at it from another angle we may conclude that the good results obtained using Eq. (6.4) justify the two approximations made i.e. the replacement of $H_c + V$ by the Hellmann potential and the omission of V_P from the equation.

VII. Summary

The main result of this paper is the formulation of a comprehensive, exact, many-valence-electron pseudopotential theory. The theory has been presented in two steps: First we derived the exact equation for the orthogonalized wave function, Eq. (3.28); then, using that equation we constructed the exact pseudopotential equation, Equation (4.4). Both equations define the best wave function for the valence electrons. While the solutions of (3.28) must be orthogonalized to the core orbitals, the solutions of (4.4) are pseudowavefunctions which do not have to satisfy any orthogonality requirements. The eigenvalue computed from either equations is the energy minimum of the valence electrons. The correlation effects between the valence electrons are fully incorporated into both equations.

As the first application of the exact theory we have shown that, the widely used and simple model

Hamiltonian of Eq. (5.1) can be derived from the exact pseudopotential equation by just two plausible approximations. We have also shown that the $P \rightarrow 1$ approximation which involves many-electron effects can be justified, in the case of atoms with two valence electrons, by accurate qualitative arguments based on perturbation theory. We expect that the exact pseudopotential equation will serve as the justification of previous calculations as well as the basis for the development of new models.

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