Pseudopotential Theory for Molecules

Levente Szasz

Department of Physics, Fordham University New York, New York 10458

(Z. Naturforsch. **32 a**, 252—263 [1977]; received January 17, 1977)

The new exact formulation of the pseudopotential theory developed in several previous publications is used to formulate a comprehensive pseudopotential theory of molecules. It is assumed that the pseudopotential theory can be applied to molecules in which there are n valence electrons plus cores which are the same in the molecule as in the separated atoms. Using the exact pseudopotential formulation it is shown that the molecular model Hamiltonian of the n valence electrons can be built up from the model Hamiltonians of the valence electrons of the separated atoms. The model Hamiltonian is written in terms of simple model potentials. For the determination of the model potentials simple rules are derived. It is shown that the model potentials, in which the many-valence-electron effects are fully taken into account can be determined using the Hartree-Fock data for the separated neutral atoms. It is shown that the molecular model Hamiltonian is removed from the exact one by two approximations which are shown to be accurate if the model potentials are properly chosen. The computational procedures are elucidated by discussing the examples of the molecules Cl_2, Hg_2 and HgH.

I. Introduction

The idea of using pseudopotentials for molecular calculations originated with Hellmann[1] and the first systematic application of pseudopotential theory to the problem of molecular binding was carried out some years ago by Szasz and McGinn[2]. Since then the pseudopotential method has been applied in many molecular calculations[3]. Although these calculations have yielded useful and accurate information they are not based on a comprehensive many-electron theory. The model Hamiltonian used in the calculations is usually a more or less satisfactory generalization of the pseudopotential model for one-valence-electron systems.

In several recent publications[4, 5] an exact pseudopotential theory has been developed by the author of this paper. In these publications a unified treatment for atoms and molecules was designed and a system with an arbitrary number of valence electrons considered. It has been shown that an exact equation for the correlated pseudowavefunction of n valence electrons can be derived for an atom or molecule. It has also been shown that the exact equation which has a surprisingly simple structure can be replaced by a simple model equation which is well suited to numerical calculations.

The purpose of the present paper is to apply the new theory mentioned above to the problem of molecular calculations, i. e. to develop a comprehensive pseudopotential theory of molecules. This will be done in the following steps. In Section II it will be defined which are the molecules to which the pseudopotential method can be applied. Taking a look at the process of molecular building *it will be shown that the exact n-valence-electron pseudopotential equation can be written down for each phase of the binding process thereby proving for the first time the applicability of the pseudopotential method in molecular calculations.* [The discussion will be presented for diatomic molecules but can be generalized easily to polyatomic molecules.] In Sections II and III it will be shown that the exact pseudopotential equation can be replaced by a very simple model equation well suited to numerical calculations. In Section III the rules for the construction of the model equation will be laid down by introducing a new type of model potential. Instead of adjusting the parameters of the model potentials to empirical data, we developed a scheme in which the model potentials of the molecular Hamiltonian are adjusted to the Hartree-Fock parameters of the separated atoms. This procedure, besides removing the semi-empirical element from the theory allows us to take into account properly the many-valence electron effects in the determination of the model potentials. Also in Section III it will be shown that viewing the difference between the model Hamiltonian and the exact Hamiltonian as a perturbation the first order perturbation energy will be negligibly small if the model potentials are chosen properly. Section IV contains a discussion of the energy relationships; here the importance of taking into account in the calculations valence-valence correlation effects clearly emerges. Section V contains a summary of the computational procedures for diatomic molecules.

The procedures are elucidated by discussing the examples of Cl_2, Hg_2 and HgH molecules. Section VI contains the summary where we concentrate on discussing the approximations involved in the theory presented in the paper.

II. The Pseudopotential Hamiltonian for Diatomic Molecules

Let us consider an atom or molecule with an arbitrary number of electrons and nuclei and let us denote the number of valence electrons by n the number of core electrons by K and let $K+n=N$. The Hartree-Fock (HF) equations for the system are

$$H_{\mathrm{F}}\,\Phi_i=\varepsilon_i\,\Phi_i\,, \quad (i=1,2,\ldots,N)\,, \tag{2.1}$$

where H_{F} is the HF Hamiltonian

$$H_{\mathrm{F}}=t+U\,. \tag{2.2}$$

In this unified treatment for atoms and molecules [5] the operator t is different for the two systems i. e. for molecules we write

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

and for atoms we put

$$t_i=-\tfrac{1}{2}\Delta_i-Z/r_i\,. \tag{2.4}$$

The notation which is in atomic units is self-explanatory. The HF potential U is given as

$$U=\sum_{s=1}^{N} U_s\,, \tag{2.5}$$

where

$$\langle 1\,|\,U_s\,|\,1'\rangle=\int \Phi_s^*(2)\,[\langle 1\,2\,|\,v\,|\,1'\,2'\rangle-\langle 1\,2\,|\,v\,|\,2'\,1'\rangle]\,\Phi_s(2')\,\mathrm{d}x_2\,\mathrm{d}x_2'\,, \tag{2.6}$$

and

$$\langle 1\,2\,|\,v\,|\,1'\,2'\rangle=\delta(1-1')\,\delta(2-2')\,(1/r_{12})\,. \tag{2.7}$$

The HF energy is

$$E_{\mathrm{F}}=\sum_{i=1}^{N}\varepsilon_i-\tfrac{1}{2}\sum_{i,j=1}^{N}\varepsilon_{ij}\,, \qquad \text{where} \qquad \varepsilon_{ij}=\langle\Phi_i\,|\,U_j\,|\,\Phi_i\rangle\,. \qquad (2.8),\ (2.9)$$

We introduce the pseudopotential method [5] with the wave function

$$\Psi_{\mathrm{T}}=(N!)^{-1/2}\,\tilde{A}\{\Phi_1(1)\ldots\Phi_K(K)\,\Psi(K+1,K+2,\ldots,N)\}\,, \tag{2.10}$$

where the first two symbols are a normalization constant and an antisymmetrizer and Ψ is a correlated n-electron pseudowavefunction subjected only to the antisymmetry and normalization requirements. As we have shown [5] the exact Ψ is given, if the core orbitals are solutions of (2.1), by the equation

$$\{H+Q\,P\}\,\Psi=E\,\Psi\,. \tag{2.11}$$

The solutions of this equation do not have to satisfy orthogonality conditions with respect to the core orbitals i. e. they are pseudowavefunctions. The meaning of the symbols are as follows:

$$H=\sum_{i=1}^{n}[H_{\mathrm{F}}(i)+V(i)]\,, \tag{2.12}$$

$$V=\sum_{s=1}^{K}|\,\Phi_s\rangle\,\langle F_s\,|\,, \tag{2.13}$$

$$Q=\tfrac{1}{2}\sum_{i,j=1}^{n}v_{ij}-\sum_{s=K+1}^{N}\;\sum_{i=1}^{n}U_s(i)\,, \tag{2.14}$$

$$P=P_1\,P_2\ldots P_n\,, \tag{2.15}$$

$$P_j\,f(j)=f(j)-\sum_{s=1}^{K}\Phi_s(j)\int\Phi_s^*(j')\,f(j')\,\mathrm{d}x_j'\,. \tag{2.16}$$

The functions F_s are arbitrary with the proper atomic or molecular symmetry. If the total energy of the system is E_{T}, the HF energy of the core is $E_{\mathrm{F}}(K)$ then the solution of (2.11) satisfies

$$E=E_{\mathrm{T}}-E_{\mathrm{F}}(K)\,. \tag{2.17}$$

We have postulated [5] that a very close approximation to the exact equation (2.11) is obtained by the $P\rightarrow 1$ ("P replaced by 1") approximation, i. e. by the equation

$$\{H+Q\}\,\Psi=E\,\Psi\,. \tag{2.18}$$

We shall base our discussions on Eq. (2.11) as well as on Eq. (2.18) and we shall show in Section III that the $P\rightarrow 1$ can be justified by accurate qualitative arguments.

Let us consider now a diatomic molecule of AB type and let us postulate that the pseudopotential model is applicable to such molecules in which the process of binding can be assumed to consist of the sequence of five configurations which are demonstrated in the Figure. Configuration 1 consist of the separated atoms A and B, which have n_1 and n_2 valence electrons and K_1 and K_2 core electrons. In

Conf. 2 the $n = n_1 + n_2$ valence electrons have moved into molecular orbitals but the two cores remain atomic. The same is true for Conf. 3 where the cores show some overlap but they are still atomic. In Conf. 4 all electrons are moving in molecular orbitals and Conf. 5 is the united atom.

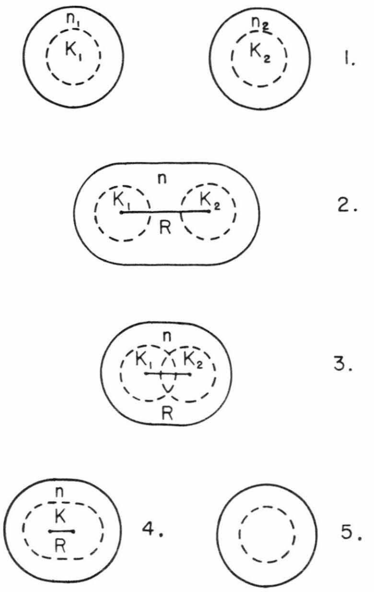

Fig. 1. The five configurations demonstrating the process of molecular binding in diatomic molecules.

The first and most important observation is that *due to the unified treatment for atoms and molecules the exact pseudopotential Eq. (2.11) can be written down for each of the five configurations. This fact constitutes the justification for the application of the pseudopotential method to molecular calculations.*

The second observation is that although Eq. (2.11) can be written down for each configuration it will be very different for each configuration; e. g. for Conf. 1 we have two equations, one for the valence electrons of atom A, one for the valence electrons of atom B; for Conf. 4 we have one equation for the valence electrons of the molecule. *We will formulate the pseudopotential method in such a way as to be applicable to Conf. 2 and 3* since we can assume that many molecules have, in the vicinity of equilibrium internuclear distance, the structure of Configuration 3.

Let us rewrite now Eq. (2.18) as follows:

$$H + Q = S + T\,, \tag{2.19}$$

where

$$S = \sum_{i=1}^{n} [H_c(i) + V(i)]\,, \tag{2.20}$$

and

$$T = \tfrac{1}{2} \sum_{i,j=1}^{n} v_{ij}\,. \tag{2.21}$$

In (2.20) the H_c is the HF operator for the core

$$H_c = t + \sum_{s=1}^{K} U_s\,. \tag{2.22}$$

Using (2.19) Eq. (2.18) takes the form

$$(S + T)\,\Psi = E\,\Psi\,. \tag{2.23}$$

The physical interpretation of this equation is simple. The operator S represents the interaction between the core and valence electrons. S includes the pseudopotentials V which prevent the valence electrons from collapsing into the core. T represents the Coulomb interaction between valence electrons. We note that like Eq. (2.11), the approximate Eq. (2.23) is also valid for an arbitrary atom or molecule and can be written down for any of the five configurations.

Now let us apply Eq. (2.23) to Conf. 1, 2 and 3. As we pass from Conf. 1 to Conf. 2 the valence electrons of the separated atoms move into the molecular orbitals of the molecule. What happens to $S + T$ in this process? Since the operator S depends only on the core orbitals the structure of this operator will be the same in Conf. 2 as it is in Conf. 1; and again the same in Conf. 3. On the other hand the operator T does not in any way depend on the core orbitals therefore this operator will simply represent the valence-valence interaction in Conf. 1 as well as in Conf. 2 and 3.

We can easily write down T for any configuration; our only problem is how to form the S. We construct S for Conf. 2 and 3 in such a way that

$$S \rightarrow S_A + S_B \tag{2.24}$$

when the internuclear distance goes to infinity i. e.

$$R \rightarrow \infty$$

and S_A and S_B are the corresponding operators for the separated atoms A and B.

We emphasize that the whole argument hinges on the fact that the structure of Eq. (2.23) is the same for all configurations (it is not specified whether S and T are referring to atoms or molecules!); the structure of Eq. (2.23) on the other hand is the direct consequence of the structure of the exact Eq. (2.11) which has also the same structure for all configurations. It is also an important feature of $S+T$ that it does not depend on the valence electron eigenvalue E or on the eigenfunction Ψ, therefore it is not affected by the transformation of Ψ from an atomic into a molecular wave function. We note also that in $S+T$ the core-valence interaction can be clearly separated from the valence-valence interaction (this is accomplished by the $P \rightarrow 1$ approximation).

The operators for the separated atoms S_A and S_B can be written down on the basis of (2.20). Recalling that H_c is given by (2.22) and (2.4) we get

$$\begin{aligned} S_A &= \sum_{i=1}^{n_1} [H_C^A(i) + V^A(i)] \\ &= \sum_{i=1}^{n_1} \left\{ -\frac{1}{2} \Delta_i - \frac{Z_A}{r_i} + \sum_{S=1}^{K_1} U_S^A(x_i) + V^A(x_i) \right\} \\ &= \sum_{i=1}^{n_1} \left\{ -\frac{1}{2} \Delta_i + h_C^A(x_i) \right\}, \end{aligned} \tag{2.26}$$

where

$$h_C^A = -Z_A/r + \sum_{S=1}^{K_1} U_S^A + V^A, \tag{2.27}$$

is the core-valence interaction operator. Also

$$T_A = \tfrac{1}{2} \sum_{i,j=1}^{n_1} v_{ij}. \tag{2.28}$$

Using these notations (2.23) becomes for atom A:

$$(S_A + T_A) \Psi_A = E_A \Psi_A. \tag{2.29}$$

Similarly we get for atom B:

$$(S_B + T_B) \Psi_B = E_B \Psi_B \tag{2.30}$$

where

$$S_B = \sum_{i=1}^{n_2} \{ -\tfrac{1}{2} \Delta_i + h_C^B(x_i) \}, \tag{2.31}$$

and

$$h_C^B = -Z_B/r + \sum_{S=1}^{K_2} U_S^B + V^B. \tag{2.32}$$

Now for Conf. 2 and 3 we put

$$S = \sum_{i=1}^{n} \{ -\tfrac{1}{2} \Delta_i + h_C^A(x_{Ai}) + h_C^B(x_{Bi}) \}. \tag{2.33}$$

Here $n = n_1 + n_2$ and x_{Ai} and x_{Bi} are the distances of the i-th electron from center A and B. The operator (2.33) satisfies (2.24). Let R increase to infinity. Let $i = 1, \ldots, n_1$ be electrons moving to A and $i = (n_1+1) \ldots (n_1+n_2)$ be electrons moving to B. Then we see from (2.27) that

$$h_C^A(x_{Ai}) \rightarrow 0, \tag{2.34}$$

if $i = (n_1+1) \ldots (n_1+n_2)$;

and from (2.32) we get that

$$h_C^B(x_{Bi}) \rightarrow 0, \tag{2.35}$$

if $i = 1, \ldots, n_1$.

In these equations we assumed that both U_s and V decrease exponentially and we neglected the long range effects of the Coulomb potential. We obtain that (2.33) satisfies the relationship

$$\lim_{R \rightarrow \infty} S = S_A + S_B, \tag{2.36}$$

where S_A and S_B are given by (2.26) and (2.31). Finally the T operator becomes

$$T = \tfrac{1}{2} \sum_{i,j=1}^{n} v_{ij}, \tag{2.37}$$

and the equation for the pseudowavefunction of the n valence electrons in Conf. 2 and 3 will be

$$(S+T) \Psi = E \Psi. \tag{2.38}$$

where S is given by (2.33) and T by (2.37).

III. The Introduction of Model Potentials and the Justification of the Approximations

The strength of the pseudopotential method relative to full ab initio calculations lies in its simplicity. In order to put the formalism in its simplest form we introduce now a molecular model Hamiltonian which is defined as an operator replacing $S+T$ in (2.38), i. e. we assume that the ground state as well as the excited states of the molecule can be represented by the equation

$$H_M \Psi = E \Psi, \tag{3.1}$$

where

$$H_M = S_M + T. \tag{3.2}$$

Here S_M will be constructed in such a way as to replace (2.33) and T is the same as before i. e. it is given by (2.37).

Clearly (3.1) is removed from the exact pseudopotential equation by two approximations. Assuming that the molecule in the vicinity of the equilibrium internuclear distance indeed looks like Conf. 3, then Eq. (3.1) contains only two approximations namely the $P \rightarrow 1$ for the separated atoms and the replacement of S by the model operator S_M. In order to justify these two approximations we proceed as follows. First we set up the rules for the construction of S_M. It will be shown that these rules follow in an unequivocal fashion from the comparison between S and S_M. Then we shall assume that we have solved the model equations for the separated atoms. Viewing the difference between the exact pseudopotential Hamiltonian and the model Hamiltonian for the separated atoms as a perturbation we will show, using perturbation theory that, the perturbation energy in the first order is negligibly small if the model potentials are properly chosen. The two approximations will be treated as one perturbation.

We replace now (2.33) by the model operator S_M:

$$S_M = \sum_{i=1}^{n} \{ -\tfrac{1}{2} \Delta_i + V_m^A(x_{Ai}) + V_m^B(x_{Bi}) \}, \tag{3.3}$$

where V_m^B and V_m^A are model potentials replacing (2.27) and (2.32) respectively. The introduction of S_M means that the equations for the separated atoms, (2.29) and (2.30) are also replaced by the following model equations:

$$(S_M^A + T_A)\, \Psi_A = E_A\, \Psi_A, \tag{3.4}$$

and

$$(S_M^B + T_B)\, \Psi_B = E_B\, \Psi_B. \tag{3.5}$$

Here S_M^A which replaces (2.26) is given by

$$S_M^A = \sum_{i=1}^{n_1} \{ -\tfrac{1}{2} \Delta_i + V_m^A(x_i) \}, \tag{3.6}$$

and S_M^B is defined by a similar equation. Clearly (3.3) satisfies the relationship

$$\lim_{R \to \infty} S_M = S_M^A + S_M^B. \tag{3.7}$$

Now we proceed to define the properties of S_M^A and S_M^B. Let us restrict the discussion for atom A; for atom B everything is the same. The model potential V_m^A replaces (2.27). We put therefore

$$V_m^A = -Z_A/r + \sum_{S=1}^{K_1} U_S^A + V^A. \tag{3.8}$$

The equality sign means "right side replaced by left side". In order to determine the properties of V_m^A we observe that the properties of the right side which is the core HF operator plus the pseudopotential cannot be easily determined. Therefore let us add the Laplacian to both sides and introduce H_F^A the HF Hamiltonian operator for the whole atom A and we get

$$-\tfrac{1}{2}\Delta + V_m^A = H_F^A + V^A - \sum_{S=K_1+1}^{N_1} U_S^A, \tag{3.9}$$

from which we get

$$-\tfrac{1}{2}\Delta + V_m^A + \sum_{S=K_1+1}^{N_1} U_S^A = H_F^A + V^A. \tag{3.10}$$

Now consider the equation

$$(H_F^A + V^A)\, \Phi_0 = \varepsilon_0\, \Phi_0. \tag{3.11}$$

In this equation H_F^A is the HF Hamiltonian operator (2.2) and V^A is the pseudopotential (2.13). As we have shown previously [5] and as is known from earlier studies [6] the eigenvalues of this equation are the valence level solutions of (2.1). The eigenfunctions of (3.11) are of the form [6]

$$\Phi_0 = \Phi_v + \sum_{s=1}^{K_1} a_s\, \Phi_s, \tag{3.12}$$

where Φ_v is one of the valence-electron solutions of (2.1), Φ_s are the HF core orbitals and

$$a_s = \langle \Phi_0 | \Phi_s \rangle. \tag{3.13}$$

Therefore we shall subject V_m^A to the requirement that the equation

$$\left(-\tfrac{1}{2}\Delta + V_m^A + \sum_{S=K_1+1}^{N_1} U_S^A \right) \Phi_0 = \varepsilon_0\, \Phi_0 \tag{3.14}$$

must reproduce the valence level HF eigenvalues exactly and the exact pseudowavefunctions (3.12) as closely as possible. We observe that the model potential V_m^A alone does not suppose to reproduce the HF energy parameters; from (3.8) it is clear that V_m^A represents the effective potential of the core, unlike H_F which contains the effective potential of the whole atom. The fact that V_m^A *plus the sum of the HF potentials for the valence states* must reproduce the HF energy parameters for the valence electrons shows clearly that V_m^A represents the effective potential of the core electrons.

We obtain an equation for atom B analogous to (3.14). Our conclusion, based on the structure of the equations (2.29) and (2.30) is that the model potentials V_m^A and V_m^B must be adjusted to match the HF energy levels of the valence electrons in the separated atoms and the eigenfunctions of the Eq. (3.14) must approximate the exact solutions of the pseudopotential Eq. (3.11) as closely as possible for both atoms.

At this point we note that the rules derived for the determination of V_m^A are such that they take fully into account the valence-valence correlation. What we mean is that our equation in the determination of V_m^A was Equation (2.29). This is an equation for the correlated pseudowavefunction Ψ_{A}. We replaced the core-valence interaction operator $h_{\mathrm{c}}^{\mathrm{A}}$ by $V_{\mathrm{m}}^{\mathrm{A}}$ and obtained the Eq. (3.4) which is again an equation for the correlated pseudowavefunction Ψ_{A}. This means that in the derivation of the rules for the determination of $V_{\mathrm{m}}^{\mathrm{A}}$ we have not made any (restrictive) assumptions about the structure of Ψ_{A} e.g. we have not used the approximation that Ψ_{A} is a Slater determinant. *The model potentials incorporate the valence-valence correlation effects because they are defined for that equation which is satisfied by the correlated pseudowavefunction* [Equation (2.29)].

Now let us assume that the model potentials have been determined. Assuming also that the model potentials are hermitian we can form a complete set from the solutions of (3.4) and we can build a perturbation calculation on these solutions in which the difference between the exact and model Hamiltonians is viewed as a perturbation. Let the solutions of (3.4) be Ψ_0 and E_0. The exact Hamiltonian for atom A is given by (2.11) [we drop the A index everywhere]:

$$\{H+QP\}\,\Psi=E\,\Psi\,. \tag{3.15}$$

Rearranging we get

$$[H+Q+Q(P-1)]\,\Psi=E\,\Psi\,. \tag{3.16}$$

Using (2.19) we can write

$$H+Q=S+T=S+S_{\mathrm{M}}-S_{\mathrm{M}}+T\,, \tag{3.17}$$

and (3.16) becomes

$$(S_{\mathrm{M}}+T+V_{\mathrm{p}}^{(1)}+V_{\mathrm{p}}^{(2)})\,\Psi=E\,\Psi\,, \tag{3.18}$$

where

$$V_{\mathrm{p}}^{(1)}=Q(P-1)\,, \tag{3.19}$$

and

$$V_{\mathrm{p}}^{(2)}=S-S_{\mathrm{M}}\,, \tag{3.20}$$

are perturbation operators. The solutions of the "unperturbed" equation [this is the same as (3.4)] are known:

$$(S_{\mathrm{M}}+T)\,\Psi_0=E_0\,\Psi_0\,. \tag{3.21}$$

In terms of the solutions of this equation we get the solutions of the exact Eq. (3.15) in the first order of perturbation theory:

$$E=E_0+E_{\mathrm{p}}^{(1)}+E_{\mathrm{p}}^{(2)}\,, \tag{3.22}$$

where

$$E_{\mathrm{p}}^{(1)}=\int \Psi_0{}^*\,V_{\mathrm{p}}{}^1\,\Psi_0\,\mathrm{d}x\,, \tag{3.23}$$

and

$$E_{\mathrm{p}}^{(2)}=\int \Psi_0{}^*\,V_{\mathrm{p}}{}^2\,\Psi_0\,\mathrm{d}x\,. \tag{3.24}$$

$E_{\mathrm{p}}^{(1)}$ is the perturbation energy arising from the $P\rightarrow 1$ approximation and $E_{\mathrm{p}}^{(2)}$ is the result of the replacement of $h_{\mathrm{c}}^{\mathrm{A}}$ by $V_{\mathrm{m}}^{\mathrm{A}}$.

Let us first consider $E_{\mathrm{p}}^{(1)}$. The Ψ_0 is a correlated solution of (3.21) which can be replaced, for the purpose of a qualitative but accurate argument by the uncorrelated product,

$$\Psi_0=\Phi_0(1)\,\Phi_0(2)\dots\Phi_0(n_1)\,, \tag{3.25}$$

where Φ_0 is a (normalized) solution of (3.14). The Φ_0 chosen this way includes the valence-valence interaction in the HF approximation as we can see by comparing (3.14) and (3.11). Using (3.19) we get

$$E_{\mathrm{p}}^{(1)}=\int \Phi_0{}^*(1)\dots\Phi_0{}^*(n_1)\,[Q(P-1)]\cdot\Phi_0(1)\dots\Phi_0(n_1)\,\mathrm{d}x\,. \tag{3.26}$$

Using (2.16) we have

$$E_{\mathrm{p}}^{(1)}=\int \Phi_0{}^*(1)\dots\Phi_0{}^*(n_1)\,Q\,\tilde{\Phi}_0(1)\dots\tilde{\Phi}_0(n_1)\,\mathrm{d}x-\int \Phi_0{}^*(1)\dots\Phi_0{}^*(n_1)\,Q\,\Phi_0(1)\dots\Phi_0(n_1)\,\mathrm{d}x\,, \tag{3.27}$$

where $\tilde{\Phi}_0$ is the orthogonalized pseudowavefunction

$$\tilde{\Phi}_0(j)=P_j\,\Phi_0(j)\,. \tag{3.28}$$

On the basis of (2.14) we can write

$$Q=\tfrac{1}{2}\sum_{i,j=1}^{n_1}v_{ij}-\sum_{i=1}^{n_1}\sum_{s=K_1+1}^{N_1}U_s(i)\,, \tag{3.29}$$

and putting this into (3.27) we get

$$E_{\mathrm{p}}^{(1)}=\tfrac{1}{2}\sum_{i,j=1}^{n_1}E(ij)-\sum_{i=1}^{n_1}\sum_{s=K_1+1}^{N_1}E_s(i)\,, \tag{3.30}$$

where the meaning of $E(ij)$ and $E_s(i)$ is evident from (3.27) and (3.29). We get e.g. for $E(1,2)$:

$$E(1,2)=\int \Phi_0{}^*(1)\,\Phi_0{}^*(2)\,v_{12}\,\tilde{\Phi}_0(1)\,\tilde{\Phi}_0(2)\,\mathrm{d}x_{12}\times\int\Phi_0{}^*(3)\,\tilde{\Phi}_0(3)\,\mathrm{d}x_3\dots\int\Phi_0{}^*(n_1)\,\tilde{\Phi}_0(n_1)\,\mathrm{d}x_{n_1}-\int \Phi_0{}^*(1)\,\Phi_0{}^*(2)\,v_{12}\,\Phi_0(1)\,\Phi_0(2)\,\mathrm{d}x_{12}\,. \tag{3.31}$$

Since both Φ_0 and the core orbitals are of the central field type we realize that $\tilde{\Phi}_0$ will have the same angular dependence as Φ_0. Let R_0 be the radial part of Φ_0 and $\tilde{R}_0$ the radial part of $\tilde{\Phi}_0$, and let

$$P_0=r\,R_0\,,\quad \tilde{P}_0=r\,\tilde{R}_0\,. \tag{3.32}$$

If the solutions of (3.14) are good approximations to the solutions of (3.11) then they have in good approximation the form of (3.12). Therefore we get

$$\Phi_0\approx\Phi_{\mathrm{v}}+\sum_{s=1}^{K_1}a_s\,\Phi_s\,, \tag{3.33}$$

and using the P operator we obtain

$$\tilde{\Phi}_0 \approx \Phi_{\rm v} . \tag{3.34}$$

Similarly we obtain

$$P_0 \approx P_{\rm v} + \sum_{s=1}^{K_1} a_s P_s , \tag{3.35}$$

and

$$\tilde{P}_0 \approx P_{\rm v} . \tag{3.36}$$

From these equations it follows that

$$P_0 \tilde{P}_0 \approx P_0{}^2 , \tag{3.37}$$

in a very good approximation. This is an accurate approximation since from (3.35) and (3.36) we see that in the valence region where the bulk of both P_0 and $\tilde{P}_0$ is located the two are exactly identical; in the core region where both P_0 and $\tilde{P}_0$ are small- because of the r, Eq. (3.32) – the relationship between P_0 and $\tilde{P}_0$ is such that $P_0{}^2$ is the average of $\tilde{P}_0{}^2$. [The latter has small oscillations while $P_0{}^2$ is a smooth function.] Equation (3.37) is exact in the valence region and a good approximation in the core region.

Now using (3.37) and the normalized character of Φ_0 we get, after integrating over the angles

$$E(1,2) = \sum_{j=1}^{\infty} a_j (\tilde{F}_j - F_j) , \tag{3.38}$$

where a_j is the coefficient resulting from the angular integration and

$$\tilde{F}_j = \int \tilde{P}_0(r_1) P_0(r_1) \tilde{P}_0(r_2) P_0(r_2) L_j(r_1 r_2) \, \mathrm{d}r_1 \, \mathrm{d}r_2 , \tag{3.39}$$

$$F_j = \int P_0^2(r_1) P_0^2(r_2) L_j(r_1 r_2) \, \mathrm{d}r_1 \, \mathrm{d}r_2 , \tag{3.40}$$

$$L_j = r_<^j / r_>^{j+1} . \tag{3.41}$$

Using (3.37) we get

$$\tilde{F}_j \approx F_j , \tag{3.42}$$

and so

$$E(1,2) \approx 0 . \tag{3.43}$$

Denoting the spherical average of the Coulomb part of $U_{\rm s}$ by $V_{\rm s}$ we get by a similar derivation

$$E_{\rm s}(1) = \int V_{\rm s} [P_0 \tilde{P}_0 - P_0{}^2] \, \mathrm{d}x , \tag{3.44}$$

and using again (3.37) we obtain

$$E_{\rm s}(1) \approx 0 . \tag{3.45}$$

A similar argument can be constructed for the exchange part of $U_{\rm s}$.

We conclude that assuming the validity of the approximation (3.37) each term in the expression for $E_p^{(1)}$, Eq. (3.30), will be negligibly small and therefore we may write that in a good approximation

$$E_p^{(1)} \approx 0 . \tag{3.46}$$

We note that strictly speaking each $E(ij)$ and $E_{\rm s}(i)$ will be different from zero but there will be considerable cancellation between the two sums of (3.30). This is true because $E(ij)$ and $E_{\rm s}(i)$ will have the same sign since they are expressions with similar structure; and from the limits of the summations we see that the number of the terms in the first sum is $\binom{n_1}{2}$ which means that it is proportional to $n_1{}^2$ and the number of the terms in the second sum is $n_1{}^2$. We can expect therefore a considerable cancellation supporting the conclusion (3.46) but it is also clear that the accuracy of the $P \rightarrow 1$ approximation declines as the number of valence electrons increases.

We note also that the accuracy of the derivation above is the greater the smaller is the overlap between the valence electron pseudowavefunction and the core wavefunctions.

Turning to $E_p^{(2)}$ we get $S - S_{\rm M}$ (for atom A) from (2.26) and (3.6). Using (3.25) again for the unperturbed solution and taking into account (2.27) we get

$$\begin{aligned}(E_p^{(2)}/n_1) = {} & \int \Phi_0{}^* [H_{\rm F} + V] \Phi_0 \, \mathrm{d}x \\ & - \int \Phi_0{}^* [-\tfrac{1}{2} \Delta + V_{\rm m} + \sum_{s=K_1+1}^{N_1} U_s] \Phi_0 \, \mathrm{d}x .\end{aligned} \tag{3.47}$$

Now we recall that Φ_0 is the solution of Eq. (3.14) and $V_{\rm m}$ is constructed in such a way that ε_0 is the HF parameter. On the other hand Φ_0 is not an eigenfunction of $(H_{\rm F} + V)$. Let us denote the solutions of (3.11) by $\tilde{\Phi}_0$ and $\tilde{\varepsilon}_0$. We can write

$$(H_{\rm F} + V) \tilde{\Phi}_0 = \tilde{\varepsilon}_0 \Phi_0 , \tag{3.48}$$

and

$$\tilde{\varepsilon}_0 = \int \tilde{\Phi}_0{}^* [H_{\rm F} + V] \tilde{\Phi}_0 \, \mathrm{d}x . \tag{3.49}$$

Now let

$$\hat{\varepsilon}_0 = \int \Phi_0{}^* [H_{\rm F} + V] \Phi_0 \, \mathrm{d}x . \tag{3.50}$$

Using (3.50) we get for (3.47):

$$(E_p^{(2)}/n_1) = \hat{\varepsilon}_0 - \varepsilon_0 , \tag{3.51}$$

where ε_0 is the HF eigenvalue for the valence level. Now if Φ_0 would be identical with $\tilde{\Phi}_0$ then we would get

$$\hat{\varepsilon}_0 = \tilde{\varepsilon}_0 \tag{3.52}$$

and since $\tilde{\varepsilon}_0$ is also the HF eigenvalue we would get the exact equation

$$E_p^{(2)} = \tilde{\varepsilon}_0 - \varepsilon_0 = 0 . \tag{3.53}$$

Since, in general, for most of the model potentials the solution Φ_0 will not be identical with the exact $\tilde{\Phi}_0$ but only a more or less good approximation to it we can write only that depending on the degree to which the equation

$$\hat{\varepsilon}_0 \approx \tilde{\varepsilon}_0 \tag{3.54}$$

is valid we obtain

$$(E_p^{(2)}/n_1) = \hat{\varepsilon}_0 - \varepsilon_0 \approx 0 \, . \tag{3.55}$$

Summarizing the results of this section we see that the solutions of the model equation (3.21) will be accurate approximations to the solutions of the exact Eq. (3.15) if the model potentials are properly constructed. If this is the case then we get for the perturbation energies

$$E_p^{(1)} \approx 0 \, , \quad E_p^{(2)} \approx 0 \, , \tag{3.56}$$

and so

$$E \approx E_0 \, . \tag{3.57}$$

We note that in order to obtain the $E_p^{(1)} \approx 0$ result the model potential must only yield a reasonably smooth pseudowavefunction with small overlap with the core orbitals; to achieve the $E_p^{(2)} \approx 0$ result the pseudowavefunction yielded by the model potential must also approximate the exact pseudowavefunction Φ_0 closely [7].

Although the discussion of the possible model potentials is outside of the scope of this paper we note that the model potentials used by Szasz and McGinn [8] are shown to be good choices in the light of the preceding discussion. In the molecular calculations performed by Szasz and McGinn the model potential was obtained by solving exactly Eq. (3.48) and then approximating the resulting HF potentials and the pseudopotential by simple analytic expressions. This procedure yields $E_p^{(2)} = 0$ exactly at least for the ground state of the valence electron.

IV. Energy Considerations

The electronic energy levels of a diatomic molecule are computed from the Equation (3.1). The eigenvalue of that equation is related to the total energy of the molecule according to (2.17) as follows:

$$E_{\mathrm{T}} = E + E_{\mathrm{F}}(K) \, , \tag{4.1}$$

where $E_{\mathrm{F}}(K)$ is the HF energy of the core. If the physical picture underlying this formula is what we called configuration 3 then the formula for the core energy will be

$$E_{\mathrm{F}}(K) = E_{\mathrm{F}}^{\mathrm{A}} + E_{\mathrm{F}}^{\mathrm{B}} + E_{\mathrm{AB}} \, , \tag{4.2}$$

where $E_{\mathrm{F}}^{\mathrm{A}}$ and $E_{\mathrm{F}}^{\mathrm{B}}$ are the HF energies of the atomic cores and E_{AB} is the interaction between the cores in the HF approximation. Let β be the binding energy. This quantity is obtained by subtracting the total energies of atoms A and B from (4.1). We have

$$E_{\mathrm{T}}^{\mathrm{A}} = E_{\mathrm{A}} + E_{\mathrm{F}}^{\mathrm{A}} \, , \tag{4.3}$$

$$E_{\mathrm{T}}^{\mathrm{B}} = E_{\mathrm{B}} + E_{\mathrm{F}}^{\mathrm{B}} \, , \tag{4.4}$$

where E_{A} and E_{B} are the solutions of (3.4) and (3.5). Using these equations we get

$$\beta = E_{\mathrm{T}} - E_{\mathrm{T}}^{\mathrm{A}} - E_{\mathrm{T}}^{\mathrm{B}} = E - E_{\mathrm{A}} - E_{\mathrm{B}} + E_{\mathrm{AB}} \, . \tag{4.5}$$

Our first result is that the core energies drop out from the formula. The valence electron energies which appear in (4.5) can be written as the sum of the HF energies plus the correlation energies:

$$E = E_{\mathrm{F}}(n) + E_{\mathrm{c}}(n) \, , \tag{4.6}$$

$$E_{\mathrm{A}} = E_{\mathrm{F}}(n_1) + E_{\mathrm{c}}(n_1) \, , \tag{4.7}$$

$$E_{\mathrm{B}} = E_{\mathrm{F}}(n_2) + E_{\mathrm{c}}(n_2) \, . \tag{4.8}$$

Using these equations we get

$$\beta = E_{\mathrm{F}}(n) - E_{\mathrm{F}}(n_1) - E_{\mathrm{F}}(n_2) + E_{\mathrm{c}}(n) - E_{\mathrm{c}}(n_1) - E_{\mathrm{c}}(n_2) + E_{\mathrm{AB}} \, . \tag{4.9}$$

In order to obtain accurate values for β one must calculate the HF energy $E_{\mathrm{F}}(n)$ as well as the correlation energy $E_{\mathrm{c}}(n)$ for the n valence electrons of the molecule; one must also compute the HF energies $E_{\mathrm{F}}(n_1)$ and $E_{\mathrm{F}}(n_2)$ of the outer shells of the separated atoms along with the correlation energies $E_{\mathrm{c}}(n_1)$ and $E_{\mathrm{c}}(n_2)$.

The formula for β may be simplified if the model Hamiltonian for the molecule (3.2) and the model Hamiltonian for the separated atoms (3.6) are modified in such a way as to include core-valence correlation. If that is the case then E_{A} and E_{B} can be expressed in terms of the ionization potentials. Let $I_1^{\mathrm{A}}, I_2^{\mathrm{A}}, \ldots, I_{n_1}^{\mathrm{A}}$ be the first n_1 ionization potentials for atom A and $I_1^{\mathrm{B}}, I_2^{\mathrm{B}}, \ldots, I_{n_2}^{\mathrm{B}}$ the first n_2 ionization potentials of atom B. We get

$$(-E_{\mathrm{A}}) = \sum_{j=1}^{n_1} I_j^{\mathrm{A}} \, , \tag{4.10}$$

$$(-E_{\mathrm{B}}) = \sum_{l=1}^{n_2} I_l^{\mathrm{B}} \, . \tag{4.11}$$

Using these equations and (4.6) in (4.5) we get

$$\beta = E_{\mathrm{F}}(n) + E_{\mathrm{c}}(n) + \sum_{j=1}^{n_1} I_j^{\mathrm{A}} + \sum_{l=1}^{n_2} I_l^{\mathrm{B}} + E_{\mathrm{AB}} \tag{4.12}$$

and the calculation of β is reduced to the calculation of the HF and correlation energies of the valence electrons plus the calculation of E_{AB}.

V. Summary of the Computational Procedures With Examples for Diatomic Molecules

Our basic equations for a diatomic molecule of AB type are the following. The properties of the molecule are computed from (3.1):

$$H_M \Psi = E \Psi , \tag{5.1}$$

where H_M is the model Hamiltonian

$$H_M = S_M + T , \tag{5.2}$$

where

$$S_M = \sum_{i=1}^{n} \{ -\tfrac{1}{2} \Delta_i + V_m^A(x_{Ai}) + V_m^B(x_{Bi}) \} , \tag{5.3}$$

and

$$T = \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{r_{ij}} . \tag{5.4}$$

The one-electron model potentials V_m^A and V_m^B are to be computed using the HF data for the separated atoms. They are to be determined in such a way that the eigenvalues of the equations below match the HF energy parameters for the valence electrons of the separated atoms:

$$(-\tfrac{1}{2} \Delta + V_m^A + \sum_{S=K_1+1}^{N_1} U_s^A) \Phi_0^A = \varepsilon_0^A \Phi_0^A , \tag{5.5}$$

and

$$(-\tfrac{1}{2} \Delta + V_m^B + \sum_{S=K_2+1}^{N_2} U_s^B) \Phi_0^B = \varepsilon_0^B \Phi_0^B , \tag{5.6}$$

where the U_s^A and U_s^B are the HF potentials of the valence electrons of atom A and B respectively. The pseudowavefunctions Φ_0^A and Φ_0^B should also approximate the outer loop of the corresponding HF functions as closely as possible and have as small an overlap with the core orbitals as possible.

Examples. The computational procedures can be elucidated by a few randomly selected examples. Let us consider the molecule Cl_2. Here A = B and the atomic configurations are

$$\underbrace{(1s)^2\,(2s)^2\,(2p)^6}_{\text{core}} \qquad \underbrace{(3s)^2\,(3p)^5}_{\text{valence}} \tag{5.7}$$

In order to decide which electrons participate in the binding we look at the HF density distributions of the separated atoms[9] and those electrons which show strong overlap at the experimental internuclear distance R_0 will be valence electrons[2]. For Cl_2 we have[10]

$$R_0 = 1.988 \text{ a. u.} . \tag{5.8}$$

The (3s) and (3p) show strong overlap at this distance therefore we designate these as valence electrons as indicated in (5.7). The number of valence electrons in the molecule will be $n = 7 + 7 = 14$. This result agrees with the description of Herzberg[11] who described the ground state of the molecule as

$$K\,K\,L\,L\,(\sigma_g\,3s)^2\,(\sigma_u\,3s)^2\,(\sigma_g\,3p)^2\,(\pi_u\,3p)^4\,(\pi_g\,3p)^4 . \tag{5.9}$$

We must next set up the equations for the model potentials V_m. The equation is (5.5) and the HF potentials in it are the (3s) and (3p) potentials. For the purpose of a demonstration let us replace U_s by the spherically symmetric Coulomb potentials, i. e. let us put

$$U_{3s} \approx \frac{Y_0\,(3s, 3s \mid r_1)}{r_1} = \int_0^\infty P^2(3s \mid r_2)\, L_0(r_1\, r_2)\, dr_2 , \tag{5.10}$$

and

$$U_{3p} \approx \frac{Y_0\,(3p, 3p \mid r_1)}{r_1} = \int_0^\infty P^2\,(3p \mid r_2) L_0(r_1\, r_2)\, dr_2 , \tag{5.11}$$

In these formulas the Y_0 is the Hartree potential function the $P(3s)$ and $P(3p)$ are the 3s and 3p HF functions and L_0 is given by (3.41).

Choosing a Hellman type potential for V_m and using (5.10) and (5.11) we get the equation for V_m:

$$\left[-\frac{1}{2} \Delta - \frac{Z}{r} + A \frac{e^{-2\varkappa r}}{r} + \frac{2}{r} Y_0\,(3s, 3s \mid r) + \frac{5}{r} Y_0\,(3p, 3p \mid r) \right] \Phi_0 = \varepsilon_0\, \Phi_0 , \tag{5.12}$$

where $Z = 7$ is the charge of the core and A and $\varkappa$ are adjustible parameters. These are to be determined from the requirement that the eigenvalues of (5.12) match the (3s) and (3p) HF parameters which are[9]

$$\begin{aligned} \varepsilon_{3s} &= -1.0729 \text{ a. u.} , \\ \varepsilon_{3p} &= -0.5064 \text{ a. u.} . \end{aligned} \tag{5.13}$$

Having obtained the A and $\varkappa$ the molecular model Hamiltonian becomes

$$H_M = \sum_{i=1}^{14} \left\{ -\frac{1}{2} \Delta_i - \frac{Z}{r_{Ai}} + A \frac{e^{-2\varkappa r_{Ai}}}{r_{Ai}} - \frac{Z}{r_{Bi}} + A \frac{e^{-2\varkappa r_{Bi}}}{r_{Bi}} \right\} + \frac{1}{2} \sum_{i,j=1}^{14} \frac{1}{r_{ij}} , \tag{5.14}$$

and the equation to be solved is (5.1).

About the approximate solution of (5.1) we wish to make the following observations. The equation can be solved by the LCAO-MO method or – since the formula (4.12) shows that the valence-valence correlation is important – it can be solved by including electron correlation in the pseudowavefunction either through configuration interaction or through interelectronic coordinates or through some other method. Whichever method is chosen for the solution it can be carried out as if the cores would not exist i. e. one has to compute the lowest eigenvalue of (5.1). In other words regardless whether the chosen solution is an LCAO or a correlated wave function it is a pseudowavefunction which does not need to be orthogonal to the core orbitals. In order to emphasize this point we note that it is more consistent to write the configuration of the molecule as

$$(\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 1p)^2 (\pi_u 1p)^4 (\pi_g 1p)^4 \qquad (5.15)$$

where the $(\sigma_g 1s)$ molecular orbital is a linear combination of atomic orbitals formed from the lowest "s" solutions of the atomic model Eqs. (5.5) and (5.6); the $(\pi_u 1p)$ is an MO formed from the lowest atomic "p" solutions etc. In practical calculations these atomic orbitals do not need to be the exact solutions of (5.5) and (5.6) but can be nodeless Slater type functions or linear combinations of such functions. The remarks above apply equally to a CI calculation as well as to the calculation of a correlated wave function in which interelectronic coordinates are included.

Next let us consider the molecules Hg_2 and HgH. The atomic configuration of Hg is

$$\text{KLMNO(spd)}(6s)^2 .$$

We assume that the (6s) electrons are the valence electrons i. e. we have for the Hg_2 $n_1 = n_2 = 2$. The equation for the model potential becomes

$$\left(-\tfrac{1}{2}\Delta + V_m + \sum_{S=1}^{2} U_s\right)\Phi_0 = \varepsilon_0 \Phi_0 , \qquad (5.17)$$

or

$$\left(-\frac{1}{2}\Delta + V_m + \frac{2}{r} Y_0(6s, 6s \mid r)\right)\Phi_0 = \varepsilon_0 \Phi_0 . \qquad (5.18)$$

The eigenvalue of this equation must match the HF energy parameter for the (6s) level which is [9]

$$\varepsilon_{6s} = -0.2610 \text{ a. u.} \qquad (5.19)$$

We have only one HF parameter to match therefore we have enough data only for a one-parameter V_m. The original prescription for V_m specified that V_m should match the filled and unfilled valence levels of the HF equations. Since in general, the HF calculations are performed only for the filled orbitals we might choose an alternative procedure. Observing that the number of valence electrons is small in the separated atoms (relative to the size of the core) we might assume that the core orbitals in the atomic cores of the molecule will not be the orbitals of the neutral atoms but the orbitals of the Hg^{++} ion ("positive core approximation"). If the number of valence electrons is small the difference between the two kinds of core orbitals is small; it is certainly not negligible if we have a larger number of valence electrons. As we have shown [4], in this case the model potential satisfies the equation

$$\left(-\tfrac{1}{2}\Delta + V_m\right)\Phi_0 = \varepsilon_0 \Phi_0 , \qquad (5.20)$$

where ε_0 must match the energy levels in the field of the Hg^{++} ion for which we might use the experimental values of the Hg^+ spectrum. [In this case the V_m will include core valence correlation.] Finally we get for the 4 valence electrons of the molecule the model Hamiltonian

$$H_M = \sum_{i=1}^{4}\left\{-\frac{1}{2}\Delta_i + V_m(x_{Ai}) + V_m(x_{Bi})\right\} + \frac{1}{2}\sum_{i,j=1}^{4}\frac{1}{r_{ij}} , \qquad (5.21)$$

and the configuration of the valence electrons will be

$$(\sigma_g 1s)^2 (\sigma_u 1s)^2 . \qquad (5.22)$$

For the HgH we have A = Hg, B = H and for the Hg the model potential is the same as in the Hg_2. For the model Hamiltonian we get

$$H_M = \sum_{i=1}^{3}\left\{-\frac{1}{2}\Delta_i + V_m^A(x_{Ai}) + V_m^B(x_{Bi})\right\} + \frac{1}{2}\sum_{i,j=1}^{3}\frac{1}{r_{ij}} , \qquad (5.23)$$

where V_m^B is the Coulomb potential of the H nucleus. The electron configuration will be

$$(1s\sigma)^2 (1p\sigma) . \qquad (5.24)$$

We note that the advantages of the pseudopotential method are even more conspicuous in the case of large cores as in Hg_2 and HgH than in the case of Cl_2. We have indicated in (5.22) the MO as $(\sigma_g 1s)$; the conventional notation would be $(\sigma_g 6s)$. In a conventional LCAO calculation the valence orbitals would be 6s atomic wave functions; in our case they are modeless Slater type functions. Although these will not be necessarily (1s) functions the reduction in computational labor is significant.

VI. Summary and Discussion

We note that although the theory presented in the paper is formulated for diatomic molecules it can be easily generalized for polyatomic molecules. The important point here is that the starting equation, the exact pseudopotential Eq. (2.11) is valid for any number of valence and core electrons and for an arbitrary number of nuclei i. e. for an arbitrary polyatomic molecule.

The results of the paper may be listed as follows. The most important part is Section II where the exact pseudopotential Eq. (2.11) and the approximate Eq. (2.23) are used to set up a pseudopotential equation for molecules, Equation (2.38). Further results are the replacement of Eq. (2.38) by the much simpler Eq. (3.1) in which we introduced the model potentials. We have shown that the model Hamiltonian for the molecule, as given by (3.2) can be built up from the model Hamiltonian of the separated atoms due to the relationship (3.7) which relationship follows in a straigthforward fashion from the structure of the exact and approximate pseudopotential Eqs. (2.11) and (2.38). An inspection of the arguments leading to the relationship

$$\lim_{R\to\infty} S_{\mathrm{M}} = S_{\mathrm{M}}^{\mathrm{A}} + S_{\mathrm{M}}^{\mathrm{B}} \tag{6.1}$$

reveals that this equation follows from the exact pseudopotential equation by just the one approximation

$$P \to 1\,. \tag{6.2}$$

The rules derived for the construction of the model potentials which are formulated in connection with Eq. (3.14) are providing a reliable framework for the construction of such model potentials which will yield accurate results. A clear summary of the computational procedures is given by the equation sequence (5.1) to (5.6).

Let us now clarify what are the approximations involved in the theory presented in this paper. The model Hamiltonian (5.2) embodies two approximations. First it was assumed that the structure of the molecule in the vicinity of equilibrium internuclear distance is like in Configuration 3, i. e. the valence electrons are moving in molecular orbitals while the cores remain atomic. Using this assumption we imposed on the model Hamiltonian the requirement (2.36) according to which the core-valence interaction operator S for the molecule must become equal to the core-valence interaction operators for the separated atoms, $S_{\mathrm{A}} + S_{\mathrm{B}}$, when $R \to \infty$. This is the step which enabled us to determine the structure of the molecular model Hamiltonian from the structure of the model Hamiltonian of the separated atoms. The assumption embodied in Configuration 3 is a physical assumption. What we mean by this is that if a molecule indeed has this structure then the pseudopotential method is applicable to it; if it does not the theory is not applicable. More precisely if the structure of the molecule will resemble Configuration 3 then the theory will provide accurate results. The two *approximations* in (5.2) are the $P \to 1$ approximation and the replacement of the h_{c} operators by the model potentials V_{m}. These are *mathematical approximations* which are introduced to make the theory mathematically simple and they consist of omitting certain terms from the model Hamiltonian [the "perturbation potentials" $V_p^{(1)}$ and $V_p^{(2)}$, Eq. (3.19) and (3.20)]. We have shown that if the model potentials are properly chosen the first order perturbation energy arising from $V_p^{(1)}$ and $V_p^{(2)}$ will be negligibly small. We have also shown that the $P \to 1$ approximation is the less "severe" from the two; in order to justify the $P \to 1$ it was enough to demand that V_{m} yields a reasonably smooth pseudowavefunction. The replacement of h_{c} by the model potentials V_{m} is a more sensitive matter which requires careful study and comparison between h_{c} and V_{m}. Although the detailed study of model potentials is outside of the scope of this paper we note that the discussions of Section III provide the guidelines for the choice of V_{m} for any given core-valence operator h_{c}. Since we now know the exact pseudopotential Hamiltonian Eq. (2.11) the accuracy of any model potential can be determined by viewing the difference as a perturbation and applying the perturbation theory.

---

[1] H. Hellmann, J. Chem. Phys. **3,** 61 [1935].

[2] L. Szasz and G. McGinn, J. Chem. Phys. **45,** 2898 [1966].

[3] See e. g. J. N. Bardsley, "Pseudopotentials", Case Studies in Atomic Physics, North Holland, Amsterdam 1974.

[4] L. Szasz and L. Brown, J. Chem. Phys. **63,** 4560 [1975]; **65,** 1393 [1976].

[5] L. Szasz, J. Chem. Phys. to be published.

[6] B. Austin, V. Heine, and L. Sham, Phys. Rev. **127,** 276 [1962].

[7] It is interesting to note that the model potential introduced by Hellmann which has been used in some very accurate calculations does not satisfy this requirement. The Hellmann potential yields good results probably because it is an accurate average of the exact pseudopotential. See the discussion of the Hellmann potential in Ref. 2 and 3.

[8] L. Szasz and G. McGinn, J. Chem. Phys. **48,** 2997 [1968].

[9] C. F. Fischer, Atomic Data **4,** 301 [1972].

[10] G. Herzberg, Molecular Spectra and Molecular Structure, D. Van Nostrand Co., New York 1951, p. 519.

[11] G. Herzberg, Op. Cit. p. 343.

[12] The equation (5.12), presented for demonstration purposes is oversimplified in three respects. First, for such a high value of the core charge it will probably be necessary to have a two-term Hellmann potential in order to produce a deeper well. (See the discussion of such cases by Szasz and McGinn, J. Chem. Phys. **42,** 2363 [1965].) Secondly, it is known that strictly speaking V_m must be an angular momentum dependent operator (Reference [2]). Thirdly, while the HF potential cancels the self-Coulomb interaction of the selected valence electron the approximate potentials (5.10) and (5.11) do not do this therefore 2 or 5 in Eq. (5.12) must be reduced by 1 when we solve this equation for the s and p states respectively.