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General Analysis of Various Methods of Atoms in Molecules

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CONTENTS

1. INTRODUCTION

MOFFITT[1] has pointed out the difficulty of calculating electronic energy levels of molecules by the orbital approach and proposed a new method called method of atoms in molecules. The idea is as follows. If we calculate, for instance, the energy difference between the ${}^3\Sigma_u{}^+$ and ${}^3\Sigma_u{}^-$ states of an O_2 molecule by the molecular-orbital method, we obtain a very poor result of about 10 ev, as compared with an observed value of 2 ev. Here the ${}^3\Sigma_u{}^+$ state is mostly built up from the covalent structure $O+O$, but the ${}^3\Sigma_u{}^-$ state has essentially an ionic structure $O^+ + O^-$. If we repeat the calculation at infinite internuclear distance, then we obtain the energy of two O atoms for the ${}^3\Sigma_u{}^+$ state and the sum of energies of O^+ and O^- ions for the ${}^3\Sigma_u{}^-$ state. The discrepancy between the calculated energy difference of 20 ev and the observed one of 11.6 ev remains the same as before. Moffitt has assumed then, that the difficulty is not a molecular problem, but atomic in origin; that is, the correlation energy included in two ions O^+ and O^- is about 10 ev greater than the correlation energy in two O atoms, at both the equilibrium distance and infinite separation. The error due to omitting the correlation energy for the ${}^3\Sigma_u{}^-$ state is therefore 10 ev greater than the error for the ${}^3\Sigma_u{}^+$ state, which has appeared in both calculations. If eigenfunctions of atoms and ions are used as basis of molecular wave functions instead of orbital functions, we can eliminate the difficulty, because then the correlation energy in atoms and ions is fully included. Although eigenfunctions of atoms and ions are not available for molecular calculations, it may be possible to use a perturbation method, because the interatomic interaction is much smaller than the intra-atomic energy. In the new method, Moffitt has introduced an interatomic interaction operator.

Unfortunately, the interatomic interaction is not so small as compared with the sought for energy difference, and depends on the choice of approximate atomic functions, with which the operator is calculated. A conventional method suggested by Moffitt[2] gives quite unsatisfactory results[3] for that reason. This does not mean, however, that the method is essentially wrong or useless.[4] Several people[5,6] have revised the method and remarkably good results have been obtained by them.

As an example, we have proposed the use of correlated atomic functions as basis of a molecular problem. Here the interatomic interaction may be approximately calculated by neglecting higher terms, but the atomic energy should be evaluated more carefully. We have separated the eigenvalues of the atoms and suggested to use observed values of atomic spectra for them. Even if observed values are used, the method is not empirical, because the values are not adjustable parameters nor quantities which include an uncertainty from the physical or mathematical viewpoints; it is certain that the atomic eigenvalues obtained by quantum mechanics should be equal to the values obtained by spectroscopy.

Recently, several arguments have been given against or about these methods.[7] If we give explicit expressions of approximate wave function for molecules and integrate the molecular Hamiltonian exactly by using the wave function, we are assured that the calculated

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[1] W. Moffitt, Proc. Roy. Soc. (London) **A210**, 224, 245 (1951).

[2] W. Moffitt, Proc. Roy. Soc. (London) **A218**, 486 (1953); W. Moffitt and J. Scanlan, ibid. **A218**, 464 (1953); **A220**, 530 (1953); W. Moffitt, Repts. Progr. Phys. **17**, 173 (1954).

[3] G. W. Scherr, J. Chem. Phys. **22**, 149 (1954); A. C. Hurley, Proc. Phys. Soc. (London) **A68**, 149 (1955); A. Rahman, Physica **20**, 623 (1954).

[4] R. Pauncz, Acta Phys. Acad. Sci. Hung. **4**, 237 (1954).

[5] A. C. Hurley, Proc. Phys. Soc. (London) **A69**, 49, 301, 767 (1956).

[6] T. Arai, J. Chem. Phys. **26**, 435, 451 (1957); **28**, 32 (1958).

[7] For instance, M. Kotani et al., Ann. Rev. Phys. Chem. **9**, 245 (1958); S. Huzinaga, Prog. Theor. Phys. (Kyoto) **20**, 15 (1958).

energy is always higher than observation because of the variational principle. Then it may be possible to see the accuracy of the wave function by comparing the calculated energy with observed value. If we make an approximation in the course of calculating matrix elements, this is not necessarily true. In our method the interatomic part is approximately calculated and therefore the calculated energy could be lower than the observed value. Consequently, it is difficult to interpret our results. Even if we get reasonable results, it may happen that the accuracy of the wave function used in calculating matrix elements is not good enough, but that the calculated energy has dropped by accumulating errors due to approximation. Such questions have arisen particularly because the simple process suggested by Moffitt has turned out to be a poor approximation.

In connection with this argument, these methods are regarded as an empirical approach and their results are therefore not comparable with results obtained by nonempirical methods. Although we have suggested use of spectroscopic data for calculating atomic energies, it is not at all essential, because we can calculate atomic energies theoretically. We need more accurate energies of atoms than interatomic interaction energy, and therefore we have to use more accurate atomic functions. We could consider that spectroscopy here is a very advanced automatic computer for the atomic problem.

In this paper, we describe a method to construct atomic functions which include correlation between electrons fully. By using the atomic functions, we construct molecular wave function and calculate the energy matrix. Here we provide some devices so that we can separate the intra-atomic energy from the interatomic interaction. Up to this point, the procedure is rigorous from a mathematical viewpoint. The more basic functions are taken into our calculation, the more accurate solutions for molecules are obtained. As we describe in Sec. 2, atomic functions are expressed as linear combinations of an infinite number of basic functions and then the energy matrix for molecules can be expanded into an infinite number of terms; each of them is an energy matrix described by the same basic functions, from which the atomic functions are constructed. If we solve the atomic problem, we can evaluate in principle the energy matrix up to a desired decimal point accurately. For practical purposes however, the series expansion should cut off at a certain point. We describe several possibilities of cutting off higher terms and discuss such approximations from physical and mathematical viewpoints. From the argument it will become clear what kinds of assumptions have been made and what kinds of differences there are between various methods of atoms in molecules. The so-called nonempirical approach is also discussed by comparing it with our method. As long as orbital functions are used as basis, it is difficult to obtain any physical quantity with accuracy satisfactory in mathematical sense, because the absolute value of an energy calculated by the orbital approach is far above the experimental value. By aid of an empirical assumption, we used to estimate the accuracy of the wave functions that made up orbitals. From our point of view, we discuss the physical meaning to be expected from such approximate wave functions and the reliability of *the empirical assumption* used in *the nonempirical method.*

Although our approach is a practical way to calculate simple molecules like a CO molecule and may be free from difficulties included in the traditional nonempirical method based on orbital functions, it is still too difficult to apply it to more complicated molecules or crystals. In the following paper we shall try to simplify our treatment, so that we can apply it for investigating electronic structures of larger molecules. Furthermore, we shall investigate the physical and mathematical background of semiempirical approaches, such as the Pariser and Parr method.[8] Extension of our approach to crystals will also be carried out.

2. ATOMIC WAVE FUNCTIONS

Before describing our method to calculate the electronic structure of molecules and crystals, we have to look carefully into atomic wave functions, from which the wave functions of molecules and crystals are made up. Here we neglect spin-dependent interaction, and therefore the Hamiltonian of atoms is given by

$$\mathcal{H}=\sum_{i=1}^{N}\{-(\hbar^2/2m)\nabla_i^2+V_i(r_i)\}+\tfrac{1}{2}\sum\sum_{i\neq j}(e^2/r_{ij}), \quad (2.1)$$

in which m is the electron mass; $\hbar$ is Planck's constant divided by 2π; r_{ij} is the distance between the positions of electrons i and j, and $V_i(r_i)$ is the potential function representing the interaction of electron i with the nucleus.

Because of our spin-independent Hamiltonian, the eigenfunctions Φ of atoms are separable into spin eigenfunctions and functions of positions of N electrons such that

$$\Phi=\sum_k \Theta_k\Psi_k, \quad (2.2)$$

where Θ_k are f linearly independent spin eigenfunctions of N electrons for a given spin total angular momentum S, and its z component S_z, and the functions of positions Ψ_k are defined as coefficients accompanied by spin eigenfunctions Θ_k.

The number f of independent spin functions is determined by the number of electrons N and the total spin angular momentum S. Although there is no unique set of independent spin functions, because linear com-

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[8] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953); **23**, 711 (1955); R. Pariser, ibid. **21**, 568 (1953); F. G. Fumi and R. G. Parr, ibid. **21**, 1864 (1953).

binations of them are also eigenfunctions of the spin system, the arbitrariness does not affect our discussion. As described in several papers,[9] spin functions are easily built up in certain systematical ways. Although it is impossible to obtain an explicit expression of the functions Ψ_k, we can describe them by using a complete set of functions $\psi_k(\mathcal{P}1,2\cdots N)$ of positions of N electrons, as follows:

$$\Psi_k=\sum_{\mathcal{P}}\sum_{K}\psi_K(\mathcal{P}1,2\cdots N)c_{Kk}(\mathcal{P}). \tag{2.3}$$

Here the functions $\psi_K(\mathcal{P})$ are factorized in the following way:

(1) Functions $\psi_K(\mathcal{P}_0)$, $\psi_K(\mathcal{P}_1)$, $\cdots\psi_K(\mathcal{P}_{t-1})$ with the same K, but distinguished by $\mathcal{P}_0$, $\mathcal{P}_1$, $\cdots\mathcal{P}_{t-1}$, are obtained from each other by permuting positions of electrons such that

$$\begin{aligned}\mathcal{P}\psi_K(\mathcal{P}_i1,2\cdots N)&=\psi_K(\mathcal{P}_ia_1,a_2\cdots a_N)\\&=\psi_K(\mathcal{P}_j1,2\cdots N),\end{aligned}$$

where $\mathcal{P}$, $\mathcal{P}_i$, and $\mathcal{P}_j$ are permutation operators associated with each other as follows:

$$\mathcal{P}\mathcal{P}_i=\mathcal{P}_j.$$

If we choose one of them as a standard function ψ_K therefore, all others are obtained from it by operating, one by one, independent permutation operators. Each set of functions $\psi_K(\mathcal{P}_0)$, $\psi_K(\mathcal{P}_1)$, $\cdots\psi_K(\mathcal{P}_{t-1})$ in Eq. (2.3) is replaced by newly created functions,

$$\psi_K,\quad \mathcal{P}_1\psi_K,\quad \mathcal{P}_2\psi_K\cdots\mathcal{P}_{t-1}\psi_K.$$

The number t of independent permutations will be $N!$ if the function ψ_K does not have any symmetry whatsoever and every possible permutation gives independent functions. On the other hand, if we have, for instance,

$$\mathcal{P}(12)\psi_K(123\cdots N)=\psi_K(213\cdots N)=\psi_K(123\cdots N),$$

then the permutation $\mathcal{P}(12)$ is not independent of the unit operator E, and the number t may decrease, at most into $(N-1)!$, depending upon some other symmetry observed in ψ_K.

(2) Functions ψ_K and $\psi_{K'}$ are linearly independent, such that possible values of c_K and $c_{K'}$ which satisfy the relation

$$c_K\psi_K+c_{K'}\mathcal{P}\psi_{K'}=0$$

are zero only as long as $K\neq K'$.

Because electrons are Fermi particles, the wave function Φ given by Eq. (2.2) should be antisymmetric with respect to permutation of electrons. If we separate the Kth functions ψ_K from the others in Eq. (2.3) as follows,

$$\Psi_k=\Psi_{Kk}+\Psi_k^{-K},$$

where

$$\Psi_{Kk}=\sum_{\mathcal{P}}c_{Kk}(\mathcal{P})\mathcal{P}\psi_K(1,2\cdots N),$$

$$\Psi_k^{-K}=\sum_{\mathcal{P}}\sum_{K'\neq K}c_{K'k}(\mathcal{P})\mathcal{P}\psi_{K'}(1,2\cdots N),$$

then our wave function is also separated into two:

$$\boldsymbol{\Phi}=\boldsymbol{\Phi}_K+\boldsymbol{\Phi}^{-K},$$

$$\boldsymbol{\Phi}_K=\boldsymbol{\Theta}\boldsymbol{\Psi}_K,$$

$$\boldsymbol{\Phi}^{-K}=\boldsymbol{\Theta}\boldsymbol{\Psi}^{-K}.$$

$$\boldsymbol{\Psi}_K=\left\{\begin{matrix}\Psi_{K1}\\ \Psi_{K2}\\ \vdots\\ \Psi_{Kf}\end{matrix}\right\},\quad \boldsymbol{\Psi}^{-K}=\left\{\begin{matrix}\Psi_1^{-K}\\ \Psi_2^{-K}\\ \vdots\\ \Psi_f^{-K}\end{matrix}\right\},\quad \boldsymbol{\Theta}=(\Theta_1\Theta_2\cdots\Theta_f).$$

It is easily proved that the K component $\boldsymbol{\Phi}_K$ of our wave function is also antisymmetric with respect to permutations of electrons because of the linear independence of the basic functions ψ_K, as described in (2). From this reason, together with the symmetry of spin eigenfunctions, a set of the t functions $\mathcal{P}\psi_K$ described in (1) is not entirely independent in our wave function Φ, but only $r(r\leq f)$ of them are independent. We prove this in the following.

At first, we separate the permutation operator $\mathcal{P}$ into two parts $\mathcal{P}_\sigma$ and $\mathcal{P}_\pi$, where $\mathcal{P}_\sigma$ is an operator for permuting spin coordinates and $\mathcal{P}_\pi$ is the corresponding operator which permutes coordinates of positions of electrons. Then we have

$$\mathcal{P}\boldsymbol{\Phi}_K=\boldsymbol{\varepsilon}\boldsymbol{\Phi}_K=\mathcal{P}_\sigma\boldsymbol{\Theta}\mathcal{P}_\pi\boldsymbol{\Psi}_K, \tag{2.4}$$

where

$$\begin{aligned}\boldsymbol{\varepsilon}&=1, &&\text{for even permutations}\\ \boldsymbol{\varepsilon}&=-1, &&\text{for odd permutations,}\end{aligned}$$

and each element $\mathcal{P}_\sigma\Theta_k$ of $\mathcal{P}_\sigma\boldsymbol{\Theta}$ can be expressed linearly in terms of f original spin eigenfunctions Θ_k:

$$\mathcal{P}_\sigma\Theta_k=\sum_{h=1}^{f}\Theta_hV_{hk}(\mathcal{P}),$$

because $\boldsymbol{\Theta}$ is a complete set of spin functions for given S and S_z, and is commutative with $\mathbf{S}^2$ and $\mathbf{S}_z$. Then we have

$$\mathcal{P}_\sigma\boldsymbol{\Theta}=\boldsymbol{\Theta}\mathbf{V}(\mathcal{P}). \tag{2.5}$$

By inserting the relation (2.5) into Eq. (2.4), it is found that

$$\boldsymbol{\Phi}_K=\boldsymbol{\varepsilon}\boldsymbol{\Theta}\mathbf{V}(\mathcal{P})\mathcal{P}_\pi\boldsymbol{\Psi}_K.$$

Comparing the equation with $\boldsymbol{\Phi}_K=\boldsymbol{\Theta}\boldsymbol{\Psi}_K$, we have

$$\mathcal{P}_\pi\boldsymbol{\Psi}_K=\boldsymbol{\varepsilon}\mathbf{V}(\mathcal{P}^{-1})\boldsymbol{\Psi}_K=\mathbf{U}^{\mathrm{tr}}(\mathcal{P})\boldsymbol{\Psi}_K, \tag{2.6}$$

where $\mathbf{U}(\mathcal{P})=\boldsymbol{\varepsilon}\mathbf{V}^{\mathrm{tr}}(\mathcal{P}^{-1})$ is an irreducible representation matrix of the permutation group. $\mathbf{U}^{\mathrm{tr}}(\mathcal{P})$ here means

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[9] For instance, M. Kotani et al., *Table of Molecular Integrals* (Maruzen Company, Ltd. Tokyo, Japan, 1955).

a transpose of $\mathbf{U}(\mathcal{P})$. The functions Ψ_{Kk} are therefore linear combinations of ψ_K, $\mathcal{P}_1\psi_K\cdots\mathcal{P}_{t-1}\psi_K$ and should satisfy Eq. (2.6). It is obvious that a set of functions

$$\Psi_{Kkh}=\sum_{\mathcal{P}}\bar{U}_{kh}(\mathcal{P})\mathcal{P}\psi_K \qquad h=1,2\cdots r,\, r\leq f \quad (2.7)$$

is a satisfactory solution. Here $\bar{U}_{Kh}(\mathcal{P})$ is a kh element of a Hermitian conjugate $\mathbf{U}\dagger(\mathcal{P})$ of $\mathbf{U}(\mathcal{P})$. The spin-orbit functions $\mathbf{\Phi}_K$ are given by the following row matrix:

$$\mathbf{\Phi}_K=\mathbf{\Theta}\mathbf{\Psi}_K \quad \text{or} \quad \Phi_{Kh}=\sum_k\Theta_k\Psi_{Kkh}, \quad h=1,2\cdots r. \quad (2.8)$$

The r functions thus obtained are linearly independent. If ψ_K does not have any symmetry, then r may be equal to f and $\mathbf{U}(\mathcal{P})$ may be obtained from $\mathbf{V}(\mathcal{P})$ by the relation (2.6). If there exists some symmetry in ψ_K, some of the functions ψ_{Kh} may disappear. In order to eliminate such cases, we have to omit the corresponding part of $\mathbf{U}(\mathcal{P})$ matrices to make reduced ones. Such a technique has been discussed elsewhere.[10]

From each of the basic functions ψ_K, we can generate r_K independent functions Φ_{Kh}. The number r_K depends on the symmetry of ψ_K but cannot exceed f. If we take all these functions obtained from every possible ψ_K used in Eq. (2.3), they may become a complete set of functions for spin and position coordinates of N electrons associated with a given S and S_z. The formal solution is then given by

$$\Phi=\sum_K\sum_h\Phi_{Kh}c_{Kh}, \quad (2.9)$$

where the coefficients c_{Kh} are obtained by minimizing the energy. By defining Ψ_k as

$$\Psi_k=\sum_K\sum_h\Psi_{Kkh}c_{Kh}, \quad (2.10)$$

it is found that

$$\Phi=\sum_k\Theta_k\Psi_k. \quad (2.11)$$

The function Φ is an exact eigenfunction of an atom and it is built up from an infinite series of position coordinates functions $\psi_0, \psi_1\cdots\psi_K\cdots$. If we use only one of them, we obtain r approximate functions. For instance,

$$\Phi_{Ki}=\sum_h\Phi_{Kh}c_{Kh}{}^i, \qquad i=1,2,\cdots r. \quad (2.12)$$

Then

$$\Phi=\sum_K\sum_i\Phi_{Ki}c_{Ki}. \quad (2.13)$$

We define Φ_0 as the function obtained from ψ_0 and the best approximation among Φ_{Ki} to the atomic eigenfunction Φ. If we build ψ_0 from a product of orbitals and choose the orbitals suitably so that Φ_0 gives an optimum energy, then Φ_0 will be the Hartree-Fock function and the coefficient c_0 corresponding to Φ_0 in the exact function will be dominant. That is,

$$c_0\approx1, \qquad |c_K|\ll1, \qquad K\neq0. \quad (2.14)$$

For convenience in the later discussion, we define a primitive function ${}^\vartheta\Phi$ or ${}^\vartheta\Psi_k$ as a function obtained from Eqs. (2.10) and (2.11) by replacing Ψ_{Kkh} with ψ_K as follows:

$${}^\vartheta\Psi_k=\sum_K\psi_Kc_{Kk}, \quad (2.15)$$

$${}^\vartheta\Phi=\sum_k\Theta_k{}^\vartheta\Psi_k. \quad (2.16)$$

In case only the first term ψ_0 of the summation (2.15) is used, we obtain the primitive function of the Hartree-Fock function such that

$${}^\vartheta\Psi_{0k}=\psi_0c_{0k}, \quad (2.17)$$

$${}^\vartheta\Phi_0=\sum_k\Theta_k{}^\vartheta\Psi_{0k}. \quad (2.18)$$

As the primitive function

$${}^\vartheta\Psi_{0k}(1,2\cdots N)=\psi_0(1,2\cdots N)c_{0k}$$

is built up from a product of orbitals as follows,

$$\psi_0(1,2\cdots N)=\phi_1(1)\phi_2(2)\cdots\phi_n(N),$$

each electron is associated with an orbital in ${}^\vartheta\Phi_0$ or ${}^\vartheta\Psi_{0k}$. For instance, electron 1 is located in orbital 1, electron 2 in orbital 2, and so on. In ${}^\vartheta\Psi_k$, the higher terms ψ_K are included and it is not so simple. However, the coefficient of the first term c_0 is dominant, as shown in Eq. (2.14), and then each electron can still be associated mainly with one orbital as in ${}^\vartheta\Psi_{0k}$. The charge distribution described by ${}^\vartheta\Psi_k$ or ${}^\vartheta\Phi$ is also approximately obtained by ${}^\vartheta\Psi_{0k}$ or ${}^\vartheta\Phi_0$.

In the exact eigenfunction, electrons are indistinguishable and each of them is not associated with a particular orbital. However, its primitive function ${}^\vartheta\Phi$ can be treated as if it is built from a simple product of orbitals, and therefore it is convenient to pick up a particular electron associated with a particular orbital.

3. WAVE FUNCTIONS IN MOLECULES

As we are still dealing with the spin-independent Hamiltonian, a wave function for molecules is described exactly the same as the Φ obtained for atoms by Eq. (2.11). If we could take so many basics ψ_K that the set of functions Ψ_{Kkh} generated is complete for describing the motion of N electrons in the molecules considered, then the wave function Φ can be an exact solution.

As a complete set of spin functions Θ is easily obtained, the difficulty we have here is again how to construct basic functions ψ_K of positions of N electrons, which will converge more quickly so that we may expect a result within satisfactory limits of error, even if we cut off the series of functions ψ_K at a certain

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[10] See reference 9; also T. Arai (unpublished).

term and neglect the higher terms. There are no functions which can be handled up to an infinite limit for our problem nor is there a mathematical technique to expand wave functions Ψ_{Kkh} by a limited number of functions, which are manageable for integrating the Schrödinger equation.

At first, we consider a case where the basic functions for a molecule are constructed from products of spin-free functions of the atoms, from which the molecule is made up. For simplifying explanation and notation, we consider a diatomic molecule, made up from atoms A and B. This does not imply any difficulty of extending our discussion to polyatomic molecules. Then we may write

$$\psi_{PQk}(1,2\cdots N_A+N_B)$$
$$=\Psi_{k'}{}^{A(Q)}(1,2\cdots N_A)\Psi_{k''}{}^{B(P-Q)}(N_A+1\cdots N_A+N_B)$$
$$k=(k',k''). \quad (3.1)$$

Here, $\Psi_{k'}{}^{A(Q)}$ and $\Psi_{k''}{}^{B(P-Q)}$ are defined in Eq. (2.10). A spin-free part of the basic function is then given by

$$\Psi_{PQkh}=\sum_{\mathcal{P}}\bar{U}_{kh}(\mathcal{P})\mathcal{P}\Psi_{k'}{}^{A(Q)}\Psi_{k''}{}^{B(P-Q)}.$$

Here it is possible to divide the permutation operator $\mathcal{P}$ into three parts as follows:

$$\mathcal{P}=\mathcal{P}_{AB}\mathcal{P}_A\mathcal{P}_B,$$

where $\mathcal{P}_A$ is an operator which permutes electrons $1,2\cdots N_A$, and a set of $\mathcal{P}_A$ is equivalent to a set of independent operators $\mathcal{P}$ for atom A and $\mathcal{P}_B$ is a corresponding one applied to atom B, whereas $\mathcal{P}_{AB}$ is one which operates between electrons $1,2\cdots N_A$ and $N_A+1\cdots N_A+N_B$.

A set of spin eigenfunctions Θ_{SMk} for N_A+N_B electrons is obtained from products of eigenfunctions for N_A+N_B electrons such that

$$\Theta_{SMk}=\sum_{M'}h_{MM'}\Theta_{S'M'k'}(1,2\cdots N_A)$$
$$\cdot\Theta_{S''M''k''}(N_A+1,\cdots N_A+N_B), \quad (3.2)$$

where $k=k'f_{S''}+k''$ and $f_{S''}$ is the number of independent $\Theta_{S''M-M'k''}$; then a representation matrix $\mathbf{U}(\mathcal{P}_B)$ is made up from one for atom B, repeating $f_{S'}$ times diagonally, where $f_{S'}$ is the number of independent $\Theta_{S'M'k'}$. A corresponding one $\mathbf{U}(\mathcal{P}_A)$ is similarly made up from one for atom A, but interchanging columns suitably to get matching order of spin functions Θ_{SMk} given by Eq. (3.2). Then it is easily found that our wave function could be factorized as follows:

$$\begin{aligned}\Phi_{PQh}&=\sum_k\Theta_{SMk}\Psi_{PQkh}\\&=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_{\mathcal{P}_A}\sum_{\mathcal{P}_B}\sum_{k}\sum_{k'}\sum_{k''}U_{kk'}(\mathcal{P}_{AB})U_{k'k''}(\mathcal{P}_A)U_{k''h}(\mathcal{P}_B)\mathcal{P}_{AB}\Theta_{k'}\mathcal{P}_A\Psi_{k'}{}^{A(Q)}\Theta_{k''}\mathcal{P}_B\Psi_{k''}{}^{B(P-Q)}\\&=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}\sum_{k'}\Theta_{k'}\Psi_{k'}{}^{A(Q)}\sum_{k''}\Theta_{k''}\Psi_{k''}{}^{B(P-Q)}\end{aligned} \quad (3.3)$$

by considering Eq. (3.2) and the structure of the representation matrices $\mathbf{U}(\mathcal{P}_A)$ and $\mathbf{U}(\mathcal{P}_B)$. As summations over $\sum_{k'}$ and $\sum_{k''}$ are wave functions of atoms A and B, respectively, we have

$$\Phi_{PQh}=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}\Phi^{A(Q)}\Phi^{B(P-Q)}. \quad (3.4)$$

From Eq. (3.2) it is found that $k=1,2\cdots f_S\leq f_{S'}\cdot f_{S''}$. As basis for molecular wave functions, we may have r independent functions $\Phi_{PQh}(h=1,2\cdots r\leq f_S)$ made up from atomic functions $\Phi^{A(Q)}$ and $\Phi^{B(P-Q)}$. By taking every possible combination of atomic functions $\Phi^{A(Q)}$ and $\Phi^{B(P-Q)}$ for atoms A and B, we are able to obtain a complete set for the molecules. Because of symmetry of molecules, however, the functions obtained from every possible P, Q, h are not linearly independent and basics of molecules may be written in a reduced form if we take suitable combinations of functions Φ_{PQh} such as

$$\Phi_{(T)}=\sum_{PQh}\Phi_{PQh}d_{PQh}{}^T.$$

Particularly if we consider ionic structures or when we are dealing with a homopolar molecule, we have to eliminate some of the basics Φ_{PQh} in order to avoid difficulties caused by overcompleteness. In practice, however, it may not be necessary to worry about it, because we are able to use only a limited number of terms, whereas the expansion of functions originating at A into those at B may need an infinite number of terms. For simplicity we may use, instead of $\Phi_{(T)}$, $\Phi_T\equiv\Phi_{PQh}$ as basics of molecules.

There are several possibilities of constructing basic functions Φ_T. We may construct basics $\psi_{K'}{}^A$ and $\psi_{K''}{}^B$ of atoms from Hylleraas-Kinoshita's functions[11] [case (I)] or from products of orbitals [case (II)]. If we take a complete set of functions as basis of each atom, then $\Phi^{A(Q)}$ and $\Phi^{B(P-Q)}$, used in Φ_T, became exact eigenfunctions of atoms A and B. Therefore, we can expect exactly the same results for a molecule by using either case (I) or (II). We specify these cases as (I_∞) and (II_∞), respectively.

It is also possible to use approximate atomic functions as basis. For instance, we may use $\Phi_0{}^{A(Q)}$ and $\Phi_0{}^{B(P-Q)}$ as defined in Eq. (2.12) by omitting the higher terms $\psi_{K'}{}^A$ and $\psi_{K''}{}^B(K'\neq0,\ K''\neq0)$. Then we can write down explicitly the molecular wave function Φ_{T0} and it is possible to calculate the energy matrix exactly. If we construct the basics $\psi_0{}^A$ and $\psi_0{}^B$ from a product

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[11] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

of the Hartree-Fock orbitals, then $\Phi_0^{A(Q)}$ and $\Phi_0^{B(P-Q)}$ are Hartree-like functions and a molecular wave function Φ_{T0} obtained is a simple Heitler-London function. We may call this case (II_0). We can construct ψ_0^A and ψ_0^B from the Hylleraas-Kinoshita functions, which are called case (I_0).

Irrespective of the basis used, we may be able to obtain an exact solution for a molecule if we take so many basics Φ_T that they constitute a complete set for the molecule. But the convergency in methods (I_0) and (II_0) is much slower than in methods (I_∞) and (II_∞). If we take a limited number of Φ_T and neglect the higher terms, we can therefore expect better results from cases (I_∞) and (II_∞) than from cases (I_0) and (II_0).

In case a limited number of basics Φ_T is used, it is thus important to introduce factors which may induce much faster convergency. For instance, the ground state of the H atom is described by the wave function $\phi_0=\pi^{-\frac{1}{2}}e^{-r}$ exactly, but the wave function of the H_2 molecule is not well described by an antisymmetrized function of the simple product $\psi_0=\phi_0^A(1)\phi_0^B(2)$. The dissociation energy calculated by this function is $D_e=2.9$ ev including the ionic term. Instead, antisymmetrizing a function $\psi_0(\rho)=\phi_0^A(1,\rho)\phi_0^B(2,\rho)$, where $\phi_0(1,\rho)=(z^3/\pi)^{\frac{1}{2}}e-{}^{zr}$, $z=1.193$, we obtain the better description of the charge distribution as well as the better energy of $D_e=4.02$ ev.[12] The function $\psi_0(\rho)$ is obtained from the original one ψ_0 by multiplying by a function $\rho_0(1,2)=\rho_0^A(1)\rho_0^B(2)$, where $\rho_0(1)=z^{\frac{3}{2}}e^{-\delta r}$.

In the orbital approach, the primitive function ${}^\vartheta\Phi$ of atoms is built up from the basics $\psi_0=\phi_1(1)\phi_2(2)\cdots\phi_n(N)$, where the ϕ's are Hartree-Fock orbitals, so that the energy of the atom is minimized and the charge distribution of electrons in the free state is well described by the function. In molecules, however, the charge distribution of the atoms is distorted by the interaction between neighboring atoms. It is therefore not advantageous to build up the molecular wave function from the atomic functions Φ_0 in the free states, but it is much better if we make up the modified atomic orbitals $\phi(i,\rho)$ in which the change in the charge distribution is taken into account, and set up the atomic function

$$\psi_0(\rho)=\phi_1(1,\rho)\phi_2(2,\rho)\cdots\phi_n(N,\rho)$$

for use as the basis of the molecular wave function. We can define the correction function ρ as follows:

$$\begin{aligned}\rho(1,2\cdots N)&=\psi_0(1,2\cdots N;\rho)/\psi_0(1,2\cdots N)\\&=\rho_1(1)\rho_2(2)\cdots\rho_n(N),\end{aligned}\tag{3.5}$$

where $\rho_1(1)=\phi_1(1,\rho)/\phi_1(1)$. The modified atomic function is then built up by

$$\Phi_0(\rho)=\sum_{\mathcal{P}}\sum_k\sum_h\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}{}^\vartheta\Psi_{0h}(\rho),\tag{3.6}$$

$${}^\vartheta\Psi_{0h}(\rho)=\rho\cdot\psi_0c_{0h}=\rho\cdot{}^\vartheta\Psi_{0h},$$

where $\rho(1,2\cdots N)\psi_0(1,2\cdots N)=\psi_0(1,2\cdots N\cdot\rho)$. The modified atomic function $\Phi_0(\rho)$ made up from the modified atomic orbitals, which can be chosen arbitrarily, is therefore interpreted as a function built up from the primitive function of a free atom multiplied by the correction function ρ.

In case an exact atomic function Φ is concerned, the primitive function ${}^\vartheta\Phi$ or ${}^\vartheta\Psi_k$ gives a close description of the charge distribution of atoms in the free state, and still each electron is associated with a definite orbital. The Hartree-Fock function is also considered a fairly good approximation to describe the charge distribution. This means that the charge distribution described by the primitive function ${}^\vartheta\Phi$ of the exact eigenfunction is approximately described by the primitive function ${}^\vartheta\Phi_0$ in the Hartree-Fock approximation. By multiplying ${}^\vartheta\Phi_0$ by the correction function ρ, the charge distribution is changed. Similarly, the charge distribution given by the exact function ${}^\vartheta\Phi$ will be changed by multiplying it by the same function ρ. Antisymmetrizing the function $\rho\cdot{}^\vartheta\Phi$, we obtain the modified atomic function,

$$\Phi(\rho)=\sum_{\mathcal{P}}\sum_k\sum_h\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}{}^\vartheta\Psi_h(\rho),$$

$${}^\vartheta\Psi_h(\rho)=\rho\cdot\sum_K\psi_Kc_{Kh}=\rho\cdot{}^\vartheta\Psi_h.\tag{3.7}$$

The modified atomic function $\Phi(\rho)$ thus obtained is therefore similar to the function $\Phi_0(\rho)$ made up from the modified atomic orbitals, and the charge distribution can be changed arbitrarily by choosing a suitable correction function ρ. The function $\Phi(\rho)$ can be defined even if the Hylleraas-type functions are used as basis. Mathematically, the function $\Phi(\rho)$ depends on the basis. If we set $\rho=1$, however, we obtain an exact eigenfunction of a free atom, regardless of the choice of basic functions. Therefore $\Phi(\rho)$ is a more generalized function than Φ.

Instead of exact atomic eigenfunctions $\Phi^{A(Q)}$ and $\Phi^{B(P-Q)}$, we therefore use the modified atomic functions $\Phi^{A(Q)}(\rho)$ and $\Phi^{B(P-Q)}(\rho)$ as basis of the molecular wave function. Then we have

$$\psi_{PQk}(\rho)=\Psi_{k'}{}^{A(Q)}(\rho)\Psi_{k''}{}^{B(P-Q)}(\rho),\tag{3.8}$$

where

$$\Psi_{k'}{}^{A(Q)}(\rho)=\sum_K\sum_h\Psi_{Kk'h}(\rho)c_{Kh},$$

$$\Psi_{Kk'h}(\rho)=\sum_{\mathcal{P}}\bar{U}_{k'h}(\mathcal{P})\mathcal{P}\rho^{A(Q)}\psi_K,$$

instead of ψ_{PQk} given by Eq. (3.1). Then

$$\begin{aligned}\Phi_T(\rho)\equiv\Phi_{PQh}=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_k\bar{U}_{hk}(\mathcal{P}_{AB})\mathcal{P}_{AB}\Phi^{A(Q)}(\rho)&\\\cdot\Phi^{B(P-Q)}(\rho),&\end{aligned}\tag{3.9}$$

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[12] S. C. Wang, Phys. Rev. **31**, 579 (1928); S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

where $\Phi^{A(Q)}(\rho)$ and $\Phi^{B(P-Q)}(\rho)$ are the modified atomic functions given by Eq. (3.7). As $\Phi^{A(Q)}$ and $\Phi^{B(P-Q)}$ are exact eigenfunctions of atoms, they satisfy the Schrödinger equation exactly. For instance,

$$\mathcal{H}^A\Phi^{A(Q)}=E^{A(Q)}\Phi^{A(Q)}.$$

But $\Phi^{A(Q)}(\rho)$ and $\Phi^{B(P-Q)}(\rho)$ are not solutions of the preceding equation. Instead, they satisfy an equation which includes a binary operator. To derive this, we introduce a function in which the primitive function ${}^{\vartheta}\Psi_h(1,\ 2\cdots N)$ and the correction function $\rho(1',\ 2'\cdots N')$ are described by independent different coordinates as follows:

$$\Phi(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho)$$
$$=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}_\psi\mathcal{P}_\rho{}^{\vartheta}\Psi_h(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho), \tag{3.10}$$

where

$${}^{\vartheta}\Psi_h(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho)$$
$$=\rho(1',\,2'\cdots N')\,{}^{\vartheta}\Psi_h(1,\,2\cdots N),$$
$${}^{\vartheta}\Psi_h(1,\,2\cdots N)=\sum_K\psi_K(1,\,2\cdots N)c_{Kh},$$

$\mathcal{P}=\mathcal{P}_\psi\mathcal{P}_\rho$, and $\mathcal{P}_\psi$ is a permutation operator of coordinates $1,\,2\cdots N$ and $\mathcal{P}_\rho$ is the corresponding permutation operator of coordinates $1'2'\cdots N'$. This function becomes equal to $\Phi(\rho)$ if the coordinates $1',\,2'\cdots N'$ are equal to $1,\,2\cdots N$, respectively. Then

$$\Phi(1,\,2\cdots N;\,\rho)$$
$$=\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\Phi(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho). \tag{3.11}$$

Then

$$\begin{aligned}\mathcal{H}^A(1,\,2,\cdots N)\Phi^{A(Q)}(1,\,2\cdots N;\,\rho)&=\mathcal{H}^A(1,\,2\cdots N)\,\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\Phi^{A(Q)}(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho)\\&=\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\{\mathcal{H}^A(1,\,2\cdots N)+\mathcal{G}^A(1,\,2\cdots N;\,1',\,2'\cdots N;\}\\&\qquad\times\Phi^{A(Q)}(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho),\end{aligned} \tag{3.12}$$

where

$$m/\hbar^2\mathcal{G}^A(1,\,2\cdots N;\,1',\,2'\cdots N')=-\sum_{i=1}^{N'}(\Delta_i'/2)-\sum_{i=1}^{N}\nabla_i\nabla_i',$$

and Δ_i' and ∇_i' operate on the coordinate i', while ∇_i operates on the coordinate i. As $\mathcal{H}^A+\mathcal{G}^A$ is symmetric and commutative with the permutation operator, we have

$$\begin{aligned}&\mathcal{H}^A(1,\,2\cdots N)\Phi^{A(Q)}(1,\,2\cdots N;\,\rho)\\&\quad=\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}_\psi\mathcal{P}_\rho\{E^{A(Q)}+\mathcal{G}^A+(\mathcal{H}^A-E^{A(Q)})\}\rho(1',\,2'\cdots N')\ {}^{\vartheta}\Psi_h(1,\,2\cdots N)\\&\quad=E^{A(Q)}\Phi^{A(Q)}(1,\,2\cdots N;\,\rho)\\&\qquad+\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}_\psi\mathcal{P}_\rho[\mathcal{G}^A(12\cdots N;\,1'2'\cdots N')\ \rho(1'2'\cdots N')\ {}^{\vartheta}\Psi_h(1,\,2\cdots N)\\&\qquad\qquad+\rho(1'2'\cdots N')\{\mathcal{H}^A(12\cdots N)-E^{A(Q)}\}{}^{\vartheta}\Psi_h(1,\,2\cdots N)].\end{aligned}$$

Therefore we can write

$$\begin{aligned}\mathcal{H}^A(1,\,2\cdots N)\Phi^{A(Q)}(1,\,2\cdots N;\,\rho)&=E^{A(Q)}\Phi^{A(Q)}(1,\,2\cdots N;\,\rho)\\&+\delta_{11'}\delta_{22'}\cdots\delta_{NN'}[\mathcal{G}^A(12\cdots N;\,1'2'\cdots N')+\{\mathcal{H}^A(1,\,2\cdots N)-E^{A(Q)}\}]\Phi^{A(Q)}(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho).\end{aligned} \tag{3.13}$$

For simplification, we write this as

$$\mathcal{H}^A\Phi^{A(Q)}(\rho)=E^{A(Q)}\Phi^{A(Q)}(\rho)+\mathcal{G}^A\Phi^{A(Q)}(\rho)+\mathcal{F}^A\Phi^{A(Q)}(\rho), \tag{3.14}$$

where

$$\mathcal{G}^A\Phi^{A(Q)}(\rho)=\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\mathcal{G}^A(1,\,2\cdots N;\,1'2'\cdots N')\Phi^{A(Q)}(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho),$$
$$\mathcal{F}^A\Phi^{A(Q)}(\rho)=\delta_{11'}\delta_{22'}\cdots\delta_{NN'}\{\mathcal{H}^A(12\cdots N)-E^{A(Q)}\}\Phi^{A(Q)}(1,\,2\cdots N;\,1',\,2'\cdots N';\,\rho).$$

4. CALCULATION OF THE ENERGY MATRIX

As in cases (I_0) and (II_0), a molecular wave function is constructed from approximate atomic functions $\Phi_0{}^{A(Q)}$ and $\Phi_0{}^{B(P-Q)}$, made up from a single term, and it is not difficult to calculate the energy matrix. In case exact atomic functions are used as basis, however, it is impossible to handle the calculation of the energy matrix exactly because an infinite number of terms is involved. We therefore have to expand the energy matrix into series of terms. The first term is so dominant that it is possible to estimate the value of the energy matrix by taking the first term only. But if it is necessary, it is possible to improve the approximation by taking more terms. To do this, we separate the energy into inter- and intra-atomic energies.

If we apply the Hamiltonian operator of a molecule to our basic wave function $\Phi_T(\rho)$ as given by Eq. (3.9), it is easily found that the Hamiltonian is separable into three parts $\mathcal{H}^A$, $\mathcal{H}^B$, and $\mathcal{V}$ as follows:

$$\mathcal{H}\Phi_T(\rho)=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}(\mathcal{H}^A+\mathcal{H}^B+\mathcal{V})$$

$$\cdot\Phi^{A(Q)}(1,2\cdots N_A;\rho)\Phi^{B(P-Q)}(N_A+1,\cdots N_A+N_B;\rho)$$

because $\mathcal{H}$ is commutative with the permutation operator $\mathcal{P}_{AB}$. In the expression

$$\Phi^{A(Q)}(1,2\cdots N_A;\rho)\Phi^{B(P-Q)}(N_A+1\cdots N_A+N_B;\rho),$$

the coordinates of the electrons $1, 2\cdots N_A$ appear only in the first part $\Phi^{A(Q)}(1, 2\cdots N_A;\ \rho)$ but not in the second part $\Phi^{B(P-Q)}(N_A+1\cdots N_A+N_B;\ \rho)$, and those of electrons $N_A+1\cdots N_A+N_B$ are in the second part $\Phi^{B(P-Q)}$ but not in the first part $\Phi^{A(Q)}$. Then $\mathcal{H}^A$ is an operator consisting of coordinates of electrons $1, 2\cdots N_A$ and equivalent to the Hamiltonian for atom A in a free state; $\mathcal{H}^B$ is the corresponding Hamiltonian for atom B, whereas $\mathcal{V}$ is an operator which depends on both atoms A and B and represents an interatomic interaction.

An energy matrix is therefore separated into three parts as follows:

$$H_{RT}=\langle R\mid\mathcal{H}\mid T\rangle=\int\Phi_R{}^*\mathcal{H}\Phi_T d\tau$$

$$=\langle R\mid\mathcal{H}^A T\rangle+\langle R\mid\mathcal{H}^B T\rangle+\langle R\mid\mathcal{V}T\rangle,\tag{4.1}$$

where

$$\langle R\mid\mathcal{L}T\rangle=\int\Phi_R{}^*\sum_{M'}h_{MM'}$$

$$\cdot\sum_{\mathcal{P}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}\mathcal{L}\Phi^{A(Q)}(\rho)\Phi^{B(P-Q)}(\rho)d\tau.$$

$$\mathcal{L}=\mathcal{H}^A,\quad\mathcal{H}^B,\quad\text{and}\quad\mathcal{V}.$$

Putting Eq. (3.14) into Eq. (4.1), we get

$$\langle R\mid\mathcal{H}\mid T\rangle=E_T\langle R\mid T\rangle+\langle R\mid\mathcal{G}T\rangle$$
$$+\langle R\mid\mathcal{F}T\rangle+\langle R\mid\mathcal{V}T\rangle,\tag{4.1$'$}$$

where

$$E_T=E^{A(Q)}+E^{B(P-Q)},\quad\mathcal{G}=\mathcal{G}^A+\mathcal{G}^B,\quad\text{and}\quad\mathcal{F}=\mathcal{F}^A+\mathcal{F}^B.$$

An energy of the molecule is obtained by solving the secular equation

$$\mid\mathbf{H}-\lambda\mathbf{S}\mid=0,\tag{4.2}$$

where $\mathbf{H}$ and $\mathbf{S}$ are matrices made up from $H_{RT}=\langle R\mid\mathcal{H}\mid T\rangle$ and

$$S_{RT}=\langle R\mid T\rangle=\int\Phi_R{}^*\cdot\Phi_T d\tau.$$

The wave function Φ is given by

$$\Phi=\sum_T\Phi_T\gamma_T,$$

where the coefficients γ_T are determined by solving the linear equations

$$\sum_T(H_{RT}-\lambda S_{RT})\gamma_T=0,\qquad R=1,2,\cdots M.\tag{4.3}$$

Here we are considering to solve the molecular problem only approximately by using a limited number M of functions Φ_T as basis. Then there is no fundamental difficulty for solving the secular equation and the linear equation, as given by Eqs. (4.2) and (4.3), if we could evaluate values of the matrices $\mathbf{H}$ and $\mathbf{S}$.

As an atomic function is made up from a linear combination of function Φ_{Kh}, consisting of single terms ψ_K as is shown in Eqs. (2.7)–(2.9), a molecular wave function given by Eq. (3.9) is also written as a linear sum of functions $\Phi_T(K'h',K''h'')$ obtained by replacing atomic functions $\Phi^{A(Q)}(\rho)\Phi^{B(P-Q)}(\rho)$ by

$$\Phi_{K'h'}{}^{A(Q)}(\rho)\Phi_{K''h''}{}^{B(P-Q)}(\rho)$$

in Eq. (3.9). Then

$$\Phi_T=\sum_K\Phi_{TK}c_K,\tag{4.4}$$

where

$$\Phi_{TK}=\Phi_T(K'h'K''h'')$$
$$=\sum_{M'}h_{MM'}\sum_{\mathcal{P}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}\Phi_{K'h'}{}^{A(Q)}(\rho)\Phi_{K''h''}{}^{B(P-Q)}(\rho),$$

$$c_K=c_{K'h'K''h''}=c_{K'h'}{}^Ac_{K''h''}{}^B.$$

Then the matrix (4.1′) is expanded as follows:

$$\langle R\mid\mathcal{H}\mid T\rangle=\sum_J\sum_K\langle R_J\mid\mathcal{H}\mid T_K\rangle c_J{}^*c_K.$$

Each term in Eq. (4.1′) is also written as

$$\langle R\mid\mathcal{L}T\rangle=\sum_J\sum_K\langle R_J\mid\mathcal{L}T_K\rangle c_J{}^*c_K.$$

Here the notation $\langle R_J\mid\mathcal{H}\mid T_K\rangle$ and $\langle R_J\mid\mathcal{L}T_K\rangle$ indicates that Φ_{TK} and Φ_{RJ} are used instead of Φ_T and Φ_R. $\langle R_J\mid\mathcal{H}\mid T_K\rangle$ and $\langle R_J\mid T_K\rangle$ are Hermitian as well as $\langle R\mid\mathcal{H}\mid T\rangle$ and $\langle R\mid T\rangle$. Even if we take the summation K, appearing in Eq. (4.4), up to a limited number K_0 of terms instead of infinite number and neglect the higher terms, the secular equation (4.2) therefore is Hermitian. But each term in $\langle R\mid\mathcal{H}\mid T\rangle$ given by Eq. (4.1′) is not Hermitian. Thus, if we take the summation K in the wave function (4.4) up to infinity and separate the matrix into terms as in Eq. (4.1′), then, if we cut off the summations appearing in, for instance, $\langle R\mid\mathcal{G}T\rangle$ and $\langle R\mid\mathcal{V}T\rangle$ at the J_0th and K_0th terms, and neglect the higher terms, but calculate others, E_T, $\langle R\mid T\rangle$, and $\langle R\mid\mathcal{F}T\rangle$, exactly by taking summations up to infinity, the approximate matrix obtained $\langle R\mid\mathcal{H}T\rangle_{\text{approx}}$ is no longer Hermitian. In order to eliminate this difficulty, we may make a skew Hermitian and add it to Eq. (4.1′) such that

$$\begin{aligned}\langle R \mid \mathcal{H} \mid T\rangle_{\mathrm{av}} &= \tfrac{1}{2}\{\langle R \mid \mathcal{H} \mid T\rangle + \langle T \mid \mathcal{H} \mid R\rangle\} \\ &= \tfrac{1}{2}(E_T+E_R)\langle R \mid T\rangle + \tfrac{1}{2}\{\langle R \mid \mathcal{G}T\rangle + \langle T \mid \mathcal{G}R\rangle\} \\ &\quad + \tfrac{1}{2}\{\langle R \mid \mathcal{F}T\rangle + \langle T \mid \mathcal{F}R\rangle\} \\ &\quad + \tfrac{1}{2}\{\langle R \mid \mathcal{V}T\rangle + \langle T \mid \mathcal{V}R\rangle\}, \qquad (4.5)\end{aligned}$$

where $E_T = E^{A(Q)} + E^{B(P-Q)}$ and

$$E^{A(Q)} = \int \Phi^{A(Q)*}\mathcal{H}^A\Phi^{A(Q)}d\tau.$$

$\langle R \mid \mathcal{H} \mid T\rangle_{\mathrm{av}}$ is exactly the same as $\langle R \mid \mathcal{H} \mid T\rangle$ if we take the summations in Eq. (4.4) up to the infinite limit, and we can obtain exactly the same solution as before. Here each of the expressions $\frac{1}{2}(E_T+E_R)\langle R \mid T\rangle$, $\frac{1}{2}\{\langle R \mid \mathcal{L}T\rangle + \langle T \mid \mathcal{L}R\rangle\}$, $\mathcal{L}=\mathcal{F}$, $\mathcal{G}$, and $\mathcal{V}$ is Hermitian too. Then even if we cut off summations included in some of them at a finite point, we can always obtain a Hermitian matrix. We use this matrix throughout the article so that we can apply reasonable approximations for evaluating the value of $\langle R \mid \mathcal{H} \mid T\rangle$. The difference between $\langle R \mid \mathcal{H} \mid T\rangle$ and $\langle R \mid \mathcal{H} \mid T\rangle_{\mathrm{av}}$ is only in the ways they are factorized in case they are expanded into series as Eq. (4.4), and therefore there is no difference in physical meaning unless we apply an approximation to them.

We try to calculate our matrix elements up to a certain decimal point correctly so that we are able to estimate the accuracy. First, we examine the order of magnitude of the terms included in Eq. (4.5). Although the first term is extremely large as compared with the rest—for instance, it may be more than 4000 ev if we consider O_2—this does not imply a very precise calculation of $\langle R \mid T\rangle$. In fact, we are interested in solving the secular equation (4.2), but not in the matrix $\langle R \mid \mathcal{H} \mid T\rangle$ itself. Then

$$\begin{aligned}\langle R \mid H-\lambda \mid T\rangle_{\mathrm{av}} &= \tfrac{1}{2}(E_T+E_R-2\lambda)\langle R \mid T\rangle \\ &\quad + \tfrac{1}{2}\{\langle R \mid \mathcal{G}T\rangle + \langle T \mid \mathcal{G}R\rangle\} \\ &\quad + \tfrac{1}{2}\{\langle R \mid \mathcal{F}T\rangle + \langle T \mid \mathcal{F}R\rangle\} \\ &\quad + \tfrac{1}{2}\{\langle R \mid \mathcal{V}T\rangle + \langle T \mid \mathcal{V}R\rangle\}. \qquad (4.6)\end{aligned}$$

Here the first and last terms have the same order of magnitude—say, 5 to 20 ev times $\langle R \mid T\rangle$ for O_2—as long as we are considering lower excited structures. If $\langle R \mid T\rangle$ and $\langle R \mid \mathcal{V}T\rangle$ are evaluated with an accuracy of 0.5%, then these parts may give an error of less than ~0.1 ev. If more higher structures are needed, the perturbation method may become more useful. There we may not need very much accuracy and the convergency of the perturbation treatment may be quick. We discuss such a case later. The first term may be called an intra-atomic energy, and the last one is an inter-atomic interaction. The energy loss of atoms in molecules due to deformation ρ is obtained from the second and third terms. Their values depend on the choice of ρ. Atoms in molecules are supposed to preserve most of their own character in the free states, and therefore the deformation of the charge cloud when in molecules may not be so extraordinary. Then use of ρ, which introduces a rather small deformation, should be quite satisfactory. The energy loss due to ρ is of the order of a few ev, and an accuracy of a few percents is enough to calculate them. Of course, it is possible to introduce as ρ any function which may produce large correction terms.

(1) Atomic Energy (E_T+E_R)

Here we have to be careful about the fact that $E_T + E_R - 2\lambda$ and $\langle R \mid \mathcal{F}T\rangle$ consist of differences between large values. The first one is the difference between the sum of energies of the atoms in the free state $\frac{1}{2}(E_T+E_R)$ and the molecular energy λ. If we use Slater orbitals for calculating $\frac{1}{2}(E_T+E_R)$, we may get a large error of about 40 ev in the case of O_2. This error then appears in our final result λ. If we use N basic functions, then mathematically, errors in λ could accumulate up to $40\times N$ ev. This is too much exaggerated, because the variational method for calculating atomic energies assures that the calculated energy is always higher than the real value. Then the error $(E_{\mathrm{calc}}-E_{\mathrm{real}})$ is always positive. Besides, we know empirically that the error is almost constant for various atomic states. Although there is no mathematical proof, one assumes that the error is constant in order to be able to give some physical meaning to the results obtained by the orbital approach. This is neither correct nor satisfactory. For instance, if we calculate energy levels of the C atom by applying the orbital approach, the energy differences between levels are not given correctly, as shown in Fig. 1. This means that the error, included in the energy calculation, is not constant, but fluctuates between about 4 and 7 ev. Therefore we have to calculate this part carefully by taking higher terms:

$$\begin{aligned}E^{A(Q)} &= \int \Phi^{A(Q)*}\mathcal{H}^A\Phi^{A(Q)}d\tau \\ &= \sum_K\sum_h E_{Kh}{}^{A(Q)}c_{Kh}{}^2.\end{aligned}$$

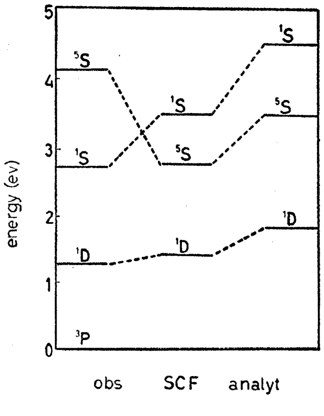

FIG. 1. Observed and calculated energy levels of the C atom. (Reproduced from the second of references 1 with the permission of the Royal Society of London.)

Calculation of atomic energy may not be so complicated as a molecular or crystal problem, but it is still difficult to obtain a satisfactory result. Apart from that, we are not primarily interested in the atomic problem. Instead, spectroscopic data give correct values for the atomic energy. The accuracy is far better than we may expect from calculated values by using an electronic computer. In fact, the energy obtained here is an eigenvalue of a much more accurate Hamiltonian, in which the spin-orbit interaction and relativistic effects are included. Therefore we can employ in our method a more accurate Hamiltonian of molecules, in which the spin-dependent part is explicitly included. The main contribution of the relativistic effect in molecules may appear in the intra-atomic part, which is treated exactly by the use of spectroscopic data. The effect on the interatomic interaction is small and is evaluated by the perturbation method.

(2) Exchange Correction Due to Deformation of Atoms $\langle R \mid \mathfrak{F}T \rangle$

In order to see the character of $\langle R \mid \mathfrak{F}T \rangle$, we recall that $\Phi^{A(Q)}$ is an eigenfunction of the Hamiltonian $\mathcal{H}^A$, which satisfies the Schrödinger equation exactly as follows:

$$0=(\mathcal{H}^A-E^{A(Q)})\Phi^{A(Q)}$$
$$=(\mathcal{H}^A-E^{A(Q)})\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\,{}^{\vartheta}\psi_h{}^A.$$

As $\mathcal{P}$ is commutative with $\mathcal{H}^A$, we find that

$$\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\{(\mathcal{H}^A-E^{A(Q)})\,{}^{\vartheta}\psi_h{}^A\}=0. \qquad (4.7)$$

By multiplying $\rho^{A(Q)}$ by the preceding equation and adding it to $\mathfrak{F}^A\Phi^{A(Q)}(\rho)$ given in Eq. (3.14), it is found that

$$\mathfrak{F}^A\Phi^{A(Q)}(\rho)$$
$$=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})[\mathcal{P}\{\rho^{A(Q)}(\mathcal{H}^A-E^{A(Q)})\,{}^{\vartheta}\psi_h{}^A\}$$
$$-\rho^{A(Q)}\{\mathcal{P}(\mathcal{H}^A-E^{A(Q)})\,{}^{\vartheta}\psi_h{}^A\}].$$

Then we may separate it into two parts:

$$\mathfrak{F}^A\Phi^{A(Q)}(\rho)=\mathfrak{F}_1{}^A\Phi^{A(Q)}(\rho)-E^{A(Q)}\mathfrak{F}_2{}^A\Phi^{A(Q)}(\rho),$$
$$\mathfrak{F}_1{}^A\Phi^{A(Q)}(\rho)$$
$$=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})(\mathcal{P}\rho^{A(Q)}-\rho^{A(Q)}\mathcal{P})\mathcal{H}^{A\vartheta}\psi_h{}^A,$$
$$\mathfrak{F}_2{}^A\Phi^{A(Q)}(\rho)=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})(\mathcal{P}\rho^{A(Q)}-\rho^{A(Q)}\mathcal{P})\,{}^{\vartheta}\psi_h{}^A. \qquad (4.8)$$

As both expressions are zero when $\mathcal{P}=E$, the $\mathfrak{F}$ term is the change of the intra-atomic exchange energy due to deformation of an atom. The main contribution $\mathfrak{F}_2{}^A$ of the change is already included in the first term $\frac{1}{2}(E_T+E_R)\langle R \mid T \rangle$ of the energy matrix (4.5) by the use of the overlap metric $\langle R \mid T \rangle$, calculated by the wave functions in deformed states instead of one obtained by functions $\rho^A\Phi^A$. The $\mathfrak{F}^A$ term is the difference between the total change $\mathfrak{F}_1{}^A$ and the main part $\mathfrak{F}_2{}^A$ and is usually expected to be very small.[13] In any case, both terms are small and do not depend appreciably on the correlation energy in atoms, because they are related to exchange interaction between different orbitals, where the correlation energy is expected to be small. The discussion given in the next section applies to this term too.

5. APPROXIMATION AND ITS ACCURACY

From the arguments just given it is clear that the energy matrix may be calculated with an accuracy satisfactory enough for obtaining wave functions and energy levels even if we cut off the series expansion (4.4) at a certain point and neglect the higher terms, as long as we calculate (E_T+E_R) very accurately. How many terms Φ_{TK} in Φ_T we should take depends on the accuracy desired and also on the molecule considered. However, it is not easy to get accurate atomic functions and, if possible, simplification is preferable for application to more complicated molecules and crystals. Such approximations are not always necessary. It may be found that our way of expanding the energy matrix is the most convenient method in a highly accurate calculation.

Here we consider case (II_∞), where orbital functions are used as basis and use only the first term in calculating the energy matrix (4.1′) except (E_T+E_R). In order to estimate the error produced by using this approximation, we assume that Hartree's function ${}^{\vartheta}\Psi_{0k}$ is the best approximate function made up from orbital functions for describing the charge distribution of the primitive function ${}^{\vartheta}\Psi_k$ of the exact eigenfunction, and that its deviation from exact one is less than a small number $\epsilon \ll 1$ (assumption):

$$\int \mid {}^{\vartheta}\Psi_k{}^{A(Q)*}\,{}^{\vartheta}\Psi_k{}^{A(Q)}-{}^{\vartheta}\Psi_{0k}{}^{A(Q)*}\,{}^{\vartheta}\Psi_{0k}{}^{A(Q)} \mid d\tau<\epsilon \qquad (5.1)$$

so that there exists a function $\phi_k{}^{A(Q)}$ which satisfies

$$\mid {}^{\vartheta}\Psi_k{}^{A(Q)}-{}^{\vartheta}\Psi_{0k}{}^{A(Q)} \mid < \tfrac{1}{2}\epsilon \mid {}^{\vartheta}\phi_k{}^{A(Q)} \mid, \qquad (5.2)$$

where ${}^{\vartheta}\phi_k{}^{A(Q)}$ is normalized in the same manner as ${}^{\vartheta}\Phi_k{}^{A(Q)}$, that is,

$$\int {}^{\vartheta}\phi_k{}^{A(Q)*}\,{}^{\vartheta}\phi_k{}^{A(Q)}d\tau=\int {}^{\vartheta}\Psi_k{}^{A(Q)*}\,{}^{\vartheta}\Psi_k{}^{A(Q)}d\tau=\sum_K c_{Kk}{}^2.$$

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[13] In case (II), the primitive function ${}^{\vartheta}\Psi_h{}^A$ is made up from Hartree-Fock orbitals ϕ_t which satisfy the equation

$$\mathcal{H}_t\phi_t=\epsilon_t\phi_t,$$

where $\mathcal{H}_t$ is the Hartree-Fock Hamiltonian. Then we can replace $\mathcal{H}^A$ in Eq. (4.8) by

$$\sum_t \epsilon_t{}^A+\sum_{t>s}\sum (r_{ts})^{-1}-\sum_t V_t{}^A$$

as shown in Eq. (5.13). $(\mathcal{P}\rho^{A(Q)}-\rho^{A(Q)}\mathcal{P})$ is expanded as Eq. (5.12). Therefore $\langle R \mid \mathfrak{F}T \rangle$ is evaluated by the use of Eq. (5.13′).

In order to support the first half of the assumption, we may refer to the work by Green et al.[14] Equation (5.1) may be written as

$$\int \mid {}^{\vartheta}\Psi_k^{A(Q)}+{}^{\vartheta}\Psi_{0k}^{A(Q)} \mid\mid {}^{\vartheta}\Psi_k^{A(Q)}-{}^{\vartheta}\Psi_{0k}^{A(Q)} \mid d\tau<\epsilon.$$

As ${}^{\vartheta}\Psi_{0k}^{A(Q)}$ is supposed to be a good approximation to ${}^{\vartheta}\Psi_k^{A(Q)}$,

$$\int \mid {}^{\vartheta}\Psi_k^{A(Q)} \mid\mid {}^{\vartheta}\Psi_k^{A(Q)}-{}^{\vartheta}\Psi_{0k}^{A(Q)} \mid d\tau$$

and

$$\int \mid {}^{\vartheta}\Psi_{0k}^{A(Q)} \mid\mid {}^{\vartheta}\Psi_k^{A(Q)}-{}^{\vartheta}\Psi_{0k}^{A(Q)} \mid d\tau$$

have values of the same order of magnitude, and therefore Eq. (5.2) is expected naturally. Here ${}^{\vartheta}\phi_k^{A(Q)}$ is also a function similar to ${}^{\vartheta}\Psi_k^{A(Q)}$ and ${}^{\vartheta}\Psi_{0k}^{A(Q)}$, except for the vicinity of nodes that may exist in ${}^{\vartheta}\Psi_{0k}^{A(Q)}$. So we can estimate the magnitude of integrals including ${}^{\vartheta}\phi_k^{A(Q)}$ by replacing it with ${}^{\vartheta}\Psi_k^{A(Q)}$ or ${}^{\vartheta}\Psi_{0k}^{A(Q)}$.

From the assumption it is naturally found that there exists a function which satisfies

$$\mid \Phi^{A(Q)}(\rho)-\Phi_0^{A(Q)}(\rho) \mid <\tfrac{1}{2}\epsilon \mid \phi^{A(Q)}(\rho) \mid \tag{5.3}$$

everywhere in space, where

$$\int \phi^{A(Q)*}\phi^{A(Q)}d\tau=1$$

and where $\phi^{A(Q)}(\rho)$ is approximated by $\Phi^{A(Q)}(\rho)$ or $\Phi_0^{A(Q)}(\rho)$ in order to estimate the magnitude of integrals involving $\phi^{A(Q)}(\rho)$. This is reasonable because

$$\int \mid \Phi^{A(Q)*}(\rho)\Phi^{A(Q)}(\rho)-\Phi^{A(Q)*}(\rho)\Phi_0^{A(Q)}(\rho) \mid d\tau=\int \mid \Phi^{A(Q)}(\rho) \mid\mid \Phi^{A(Q)}(\rho)-\Phi_0^{A(Q)}(\rho) \mid d\tau$$

$$=\int \mid \sum_{\mathcal{P}}\sum_k\sum_h \bar{U}_{kh}(\mathcal{P})\mathcal{P}\,{}^{\vartheta}\Psi_h^{A(Q)}(\rho) \mid\mid {}^{\vartheta}\Psi_k^{A(Q)}(\rho)-{}^{\vartheta}\Psi_{0k}^{A(Q)}(\rho) \mid d\tau$$

$$\leq\sum_{\mathcal{P}}\sum_k\sum_h \mid \bar{U}_{kh}(\mathcal{P}) \mid \int \mathcal{P} \mid \rho\cdot{}^{\vartheta}\Psi_h^{A(Q)} \mid \cdot\tfrac{1}{2}\epsilon \mid \rho\cdot{}^{\vartheta}\phi_k^{A(Q)} \mid d\tau\approx\tfrac{1}{2}\epsilon.$$

Therefore

$$\int \mid \Phi^{A(Q)}(\rho) \mid\mid \Phi^{A(Q)}(\rho)-\Phi_0^{A(Q)}(\rho) \mid d\tau\leq\tfrac{1}{2}\epsilon. \tag{5.4}$$

Now we estimate the magnitude of an error produced in the calculation of the matrix element (4.1′) by using the assumption mentioned previously. To do this we calculate

$$\Delta\mathcal{L}_{RT}= \mid \langle R \mid \mathcal{L}T\rangle-\langle R_0 \mid \mathcal{L}T_0\rangle \mid \tag{5.5}$$

for $\mathcal{L}=E_T-\lambda$, $\mathcal{G}$, $\mathcal{F}$, and $\mathcal{V}$. In Eq. (5.5) R_0 and T_0 represent the molecular wave functions $\Phi_{R0}(\rho)$ and $\Phi_{T0}(\rho)$ made up from approximate atomic functions $\Phi_0^{A(Q)}(\rho)$ etc. As the molecular wave functions $\Phi_R(\rho)$ and $\Phi_T(\rho)$ are constructed from atomic functions $\Phi^{A(Q')}(\rho)$, $\Phi^{B(P'-Q')}(\rho)$ and $\Phi^{A(Q)}(\rho)$, $\Phi^{B(P-Q)}(\rho)$, respectively, as is shown in Eq. (3.4), we use a notation in which composite atomic functions are specified, such as

$$\langle R \mid \mathcal{L}T\rangle\equiv\langle Q'P' \mid \mathcal{L}QP\rangle$$

$$\langle R_0 \mid \mathcal{L}T_0\rangle\equiv\langle Q_0'P_0' \mid \mathcal{L}Q_0P_0\rangle$$

where Q_0 represents $\Phi_0^{A(Q)}(\rho)$ and so on. Then we have

$$\begin{aligned}\Delta\mathcal{L}&= \mid \langle Q'P' \mid \mathcal{L}QP\rangle-\langle Q_0'P_0' \mid \mathcal{L}Q_0P_0\rangle \mid \\ &\leq \mid \langle Q'P' \mid \mathcal{L}QP\rangle-\langle Q'P' \mid \mathcal{L}QP_0\rangle \mid \\ &\quad+ \mid \langle Q'P' \mid \mathcal{L}QP_0\rangle-\langle Q'P' \mid \mathcal{L}Q_0P_0\rangle \mid \\ &\quad+ \mid \langle Q'P' \mid \mathcal{L}Q_0P_0\rangle-\langle Q'P_0' \mid \mathcal{L}Q_0P_0\rangle \mid \\ &\quad+ \mid \langle Q'P_0' \mid \mathcal{L}Q_0P_0\rangle-\langle Q_0'P_0' \mid \mathcal{L}Q_0P_0\rangle \mid .\end{aligned} \tag{5.6}$$

Therefore we estimate the order of magnitude of the four terms in Eq. (5.6) instead of Eq. (5.5). These four terms are of the same order of magnitude in the sense of the assumption made. For instance, the second term is

$$\begin{aligned}\Delta\mathcal{L}_2&= \mid \langle Q'P' \mid \mathcal{L}QP_0\rangle-\langle Q'P' \mid \mathcal{L}Q_0P_0\rangle \mid \\ &\leq \mid \langle \mid Q'P' \mid\mid \mathcal{L} \mid\mid Q-Q_0 \mid\mid P_0 \mid\rangle \mid \\ &\leq\tfrac{1}{2}\epsilon_Q \mid \langle Q'P' \mid\mid \mathcal{L} \mid \phi_QP_0\rangle \mid .\end{aligned}$$

In $\langle Q'P' \mid\mid \mathcal{L} \mid \phi_QP_0\rangle$,[15] ϕ_Q is approximated with Q, and the approximate atomic functions Q_0', P_0', and Q_0 may be used for estimating the integrals. Then we have

$$\Delta\mathcal{L}_2\lesssim(\epsilon_Q/2) \mid \langle Q_0'P_0' \mid\mid \mathcal{L} \mid Q_0P_0\rangle \mid .$$

By repeating the same argument for the other three terms in Eq. (5.6), it is easily found that

$$\Delta\mathcal{L}\leq\tfrac{1}{2}(\epsilon_R+\epsilon_T) \mid \langle R_0 \mid\mid \mathcal{L} \mid T_0\rangle \mid , \tag{5.7}$$

where $\epsilon_T=\epsilon_Q+\epsilon_P$ and $\epsilon_R=\epsilon_{Q'}+\epsilon_{P'}$.

Here we examine the signs of the operators $\mathcal{L}=E_T-\lambda$, $\mathcal{G}$, $\mathcal{F}$, and $\mathcal{V}$. The first one, $E_T-\lambda$, is simple,

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[14] L. C. Green et al., Phys. Rev. **85**, 65 (1952); **91**, 35 (1953); **93**, 273 (1954).

[15] The notation $\mid \mathcal{L} \mid$ for a differential operator here means, that the absolute value of the differentiated function is obtained.

because it is a constant throughout space. If we are considering the ground state of a stable molecule, then $E_T > \lambda$; therefore, $E_T - \lambda > 0$. The last one is written as

$$\mathcal{V} = \sum_{i \subset A} \sum_{j \subset B} \{[(e^2/r_{ij}) - (e^2/r_{Aj})] - [(e^2/r_{Bi}) - (e^2/R)]\},$$

where $\sum_{i \subset A}$ is a summation over all electrons associated with atom A. Here each term is expanded as

$$\begin{aligned} f(ij) = r_{ij}^{-1} - r_{Aj}^{-1} &= \sum_{n=1}^{\infty} (r_{Ai}^{\ n}/r_{Aj}^{\ n+1}) P_n(\cos\theta_{ij}^{\ A}), && r_{Ai} < r_{Aj}, \\ &= \sum_{n=1}^{\infty} (r_{Aj}^{\ n}/r_{Ai}^{\ n+1}) P_n(\cos\theta_{ij}^{\ A}), && r_{Ai} > A_{Aj}, \\ g(i) = r_{Bi}^{-1} - R^{-1} &= \sum_{n=1}^{\infty} (r_{Ai}^{\ n}/R^{n+1}) P_n(\cos\theta_{iB}^{\ A}), && r_{Ai} < R, \\ &= \sum_{n=1}^{\infty} (R^n/r_{Ai}^{\ n+1}) P_n(\cos\theta_{iB}^{\ A}), && r_{Ai} > R, \end{aligned} \tag{5.8}$$

where $\theta_{ij}^{\ A} = \angle iAj$. It is possible to separate terms $f_{1t}(ij)$ and $g_{1t}(i)$ which operate on $1s$ electron j from others, because the permutation operators $\mathcal{P}$ are commutative with $\mathcal{V}$, and we can consider $\mathcal{V}$ as operating on products of primitive functions of atoms, such that $\mathcal{V}^{\vartheta}\Phi^{A(Q)\vartheta}\Phi^{B(P-Q)}$. As a $1s$ electron is localized at the vicinity of a nucleus, the contribution from $r_{Ai} > R$ or $r_{Ai} > r_{Aj}$ is negligible. By neglecting the second expansion, we find that

$$\begin{aligned} f_{1s}(ij) - g_{1s}(i) &= \sum_{n=1}^{\infty} [(r_{Ai}^{\ n}/r_{Aj}^{\ n+1}) - (r_{Ai}^{\ n}/R^{n+1})] P_n(\cos\theta_{iB}^{\ A}) + \sum_{n=1}^{\infty} (r_{Ai}^{\ n}/r_{Aj}^{\ n+1}) \{P_n(\cos\theta_{ij}^{\ A}) - P_n(\cos\theta_{iB}^{\ A})\} \\ &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} (r_{Ai}^{\ n} r_{Bj}^{\ m}/R^{m+1}) [(1/R^n) + (1/R^{n-1}r_{Aj}) + \cdots + (1/r_{Aj}^{\ n})] P_n(\cos\theta_{iB}^{\ A}) P_m(\cos\theta_{jA}^{\ B}), \quad r_{Bj} < R, \\ &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} (r_{Ai}^{\ n} R^m/r_{Aj}^{\ m+1}) [(1/R^n) + (1/R^{n-1}r_{Aj}) + \cdots + (1/r_{Aj}^{\ n}) P_n(\cos\theta_{iB}^{\ A}) P_m(\cos\theta_{jA}^{\ B}), \quad r_{Bj} > R. \end{aligned} \tag{5.9}$$

If electron j is also in a $1s$ orbital, then $r_{Bj} < R$, $r_{Aj} \approx R$ and it is found that

$$f_{1s}(ij) - g_{1s}(i) = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} [(n+1) r_{Ai}^{\ n} r_{Bj}^{\ m}/R^{n+m+1}] P_n(\cos\theta_{iB}^{\ A}) P_m(\cos\theta_{jA}^{\ B}). \tag{5.10}$$

If we evaluate $g_{1s}(i)$ and $f_{1s}(ij)$ by using $1s$ orbitals, we obtain almost zero contribution, because the $1s$ orbital is spherically symmetric and the overlap between neighboring atoms is small. However, the exact wave function Φ_T is expanded as

$$\Phi_T = \sum_n \Phi_{Tn} P_n(\cos\theta_{iB}^{\ A}) P_m(\cos\theta_{jA}^{\ B}) c_{nm}$$

and then we find nonzero contribution of the g_{1s} and f_{1s} integrals. The results are written as

$$\begin{aligned} \langle R \mid (f_{1s} - g_{1s}) T \rangle &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} [(n+1)/R^{n+m+1}] \langle R_{n'm'} \mid (r_{Ai}^{\ n} r_{Bj}^{\ m}) T_{n'm''} \rangle c_{n'm'}^{\ R*} c_{n''m''}^{\ T}, && \text{if both } i \text{ and } j \text{ are in } 1s \text{ orbitals,} \\ &= \sum_{n=1}^{\infty} \langle R_{n'} \mid [(r_{Ai}^{\ n}/r_{Aj}^{\ n+1}) - (r_{Ai}^{\ n}/R^{n+1})] T_{n''} \rangle c_{n'}^{\ R*} c_{n''}^{\ T}, && \text{if electron } i \text{ is in } 1s \text{ orbital and electron } j \text{ is not in } 1s \text{ orbital.} \end{aligned}$$

Instead of Eqs. (5.9) and (5.10), we use the following expression to estimate the error (5.7) resulting from f_{1s} and g_{1s}:

$$\begin{aligned} | f_{1s}(ij) - g_{1i}(i) | &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} [(n+1)/R^{n+m+1}] \langle r_{Ai}^{\ n} \rangle \langle r_{Bj}^{\ m} \rangle, && \text{if both } i \text{ and } j \text{ are in } 1s \text{ orbital,} \\ &= \sum_{n=1}^{\infty} \langle r_{Ai}^{\ n} \rangle [\langle 1/r_{Aj}^{\ n+1} \rangle + (1/R^{n+1})], && \text{if } i \text{ is in } 1s \text{ orbital but } j \text{ is not.} \end{aligned}$$

For the other electrons, the contributions from $r_{Ai} > R$ or $r_{Ai} \rangle r_{Aj}$ are not negligible, and it is necessary to consider Eq. (5.8) explicitly in order to estimate the error correctly; also, the convergence is slow. We consider $1/r_{ij}$ and $1/r_{Aj}$ or $1/r_{Bi}$ separately. Then the interatomic interaction operator $\mathcal{V}$ is divided into three parts, such that

$$\begin{aligned}
&\mathcal{V}=\mathcal{V}_1+\mathcal{V}_2+\mathcal{V}_3\\
&\mathcal{V}_1=\tfrac{1}{2}e^2\sum_{i\subset A}^{1s}\sum_{j\subset B}|f_{1s}(ij)-g_{1s}(i)|+\tfrac{1}{2}e^2\sum_{i\subset A}\sum_{j\subset B}^{1s}|f_{1s}(ij)-g_{1s}(i)|,\\
&\mathcal{V}_2=\sum_{i\subset A}{}'\sum_{j\subset B}{}'(e^2/r_{ij})\\
&\mathcal{V}_3=-\sum_{B}\sum_{i\subset A}{}'[(Z_B-2)e^2/r_{Bi}],
\end{aligned}\tag{5.11}$$

where $\sum_{i\subset A}{}^{1s}$ is taken over the $1s$ electrons in atom A and $\sum_{i\subset A}{}'$ means a summation over all electrons in atom A except the $1s$ orbital. Then it is found that $\mathcal{V}_1>0$, $\mathcal{V}_2>0$, and $\mathcal{V}_3<0$.

In order to examine $\mathcal{G}$, we recall that ρ is a function of r and can be expressed approximately as $N\exp(-\sum_t \delta_t r_t)$, as is shown in Eq. (3.5). The primitive function ${}^{\vartheta}\Psi_{0h}$ made up from Hartree-Fock orbitals may be approximated by Slater orbitals

$$\phi_t=\phi_{n_t l_t m_t}=N_{n_t}r^{n_t-1}\exp(-z_t r_t)\,Y_{l_t m_t}(\theta\varphi).$$

Then we have

$$\begin{aligned}
\mathcal{G}\,{}^{\vartheta}\Psi_{0h}(\rho)&=(\hbar^2/m)\sum_t\{-\tfrac{1}{2}\Delta_t\rho(1,2\cdots t\cdots N)\cdot{}^{\vartheta}\Psi_{0h}(1,2\cdots t\cdots N)-\nabla_t\rho(1,2\cdots t\cdots N)\nabla_t{}^{\vartheta}\Psi_{0h}(1,2\cdots t\cdots N)\}\\
&=(\hbar^2/m)\sum_t\{-\delta_t(z_t+\tfrac{1}{2}\delta_t)+(n_t\delta_t/r_t)\}\,{}^{\vartheta}\Psi_{0h}(\rho).
\end{aligned}$$

Here z_t, δ_t, n_t, and r_t are positive and then $-\delta_t(z_t+\frac{1}{2}\delta_t)+(n_t\delta_t/r_t)>0$ if $r_t<n_t/(z_t+\frac{1}{2}\delta_t)$. For the hydrogen-like orbitals $z_t=1/n_t$. In general, $z_t<1/n_t$ and $\delta_t<z_t$. Therefore the condition for $\mathcal{G}>0$ is $r_t<2n_t$ for every electron t. Contribution from the region $r_t>2n_t$ to the $\mathcal{G}$ integral is negligible as compared with the main part, obtained inside the region $r_t<2n_t$. For estimating the error, therefore, we may assume that $\mathcal{G}>0$ for the whole space. This can be true even if we use Hartree-Fock orbitals and more complicated wave functions.

Finally, we look into the $\mathcal{F}$ integral given by Eq. (4.8). As the correction factor ρ is written as

$$\rho=N\exp(-\sum_{t=1}^{N}\delta_t r_t),$$

it is found that

$$\begin{aligned}
(\mathcal{P}\rho^{A(Q)}-\rho^{A(Q)}\mathcal{P})&=\mathcal{P}[1-\exp\{-\sum_{t=1}^{N}(\delta_{\mathcal{P}_t}-\delta_t)r_t\}]\rho^{A(Q)}\\
&=\mathcal{P}[\sum_n(-1/n!)\{-\sum_{t=1}^{N}(\delta_{\mathcal{P}_t}-\delta_t)r_t\}^n]\rho^{A(Q)},
\end{aligned}\tag{5.12}$$

where $\mathcal{P}_t$ is the number which appears in place of t after the permutation $\mathcal{P}$. The Hamiltonian $\mathcal{H}^A$ operates on the primitive function of atom A in the free state. If we use the approximate functions Φ_{T0} for estimating an error resulting from the $\mathcal{F}$ integral, the primitive function is a simple product of Hartree-Fock orbitals ϕ_t which satis- the following equation:

$$\begin{aligned}
&\mathcal{H}_t^A\phi_t^A=\epsilon_t^A\phi_t^A\\
&\mathcal{H}_t^A=-\tfrac{1}{2}\Delta_t-(Z_A/r_{At})+V_t^A\\
&V_t^A=\sum_s\int\phi_t^{A*}(s)\,(1/r_{st})\phi_t^A(s)d\tau_s+\sum_s[\sigma\phi_s^A(t)/\phi_s^A(s)\phi_t^A(t)]\int\phi_s^A(s)^*(1/r_{st})\phi_t^A(s)d\tau_s.
\end{aligned}$$

$$\sigma=1,\quad -1,\quad\text{or}\quad -\tfrac{1}{2}.$$

Then we find that

$$\begin{aligned}\mathcal{H}^{A\,\vartheta}\Psi_{0k}{}^{A}&=\Big(\sum_{t}\mathcal{H}_t{}^{A}+\sum_{t>s}\sum(1/r_{ts})-\sum_{t}V_t{}^{A}\Big){}^{\vartheta}\Psi_{0k}{}^{A}\\&=\Big(\sum_{t}\epsilon_t{}^{A}+\sum_{t>s}\sum(1/r_{ts})-\sum_{t}V_t{}^{A}\Big){}^{\vartheta}\Psi_{0k}{}^{A}.\end{aligned}\tag{5.13}$$

By the use of Eqs. (5.12) and (5.13), Eq. (4.8) is rewritten as

$$\mathfrak{F}^{A}\Phi^{A(Q)}(\rho)=f_1{}^{A}\Phi^{A(Q)}(\rho)-f_2{}^{A}\Phi^{A(Q)}(\rho)$$

$$f_1{}^{A}\Phi^{A(Q)}(\rho)=\Big(\sum_{t}\epsilon_t{}^{A}-E^{A(Q)}\Big)\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\Big[\sum_{n}(-1/n!)\Big\{-\sum_{t}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big]{}^{\vartheta}\Psi_{0k}{}^{A}$$

$$f_2{}^{A}\Phi^{A(Q)}(\rho)=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\Big[\sum_{n}(-1/n!)\Big\{-\sum_{t}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big]\Big\{\sum_{t}V_t{}^{A}-\sum_{t>s}\sum(1/r_{ts})\Big\}{}^{\vartheta}\Psi_{0k}{}^{A}.$$

Here

$$\sum_{t}\epsilon_t{}^{A}-E^{A(Q)}>0$$

and

$$\sum_{t}V_t{}^{A}-\sum_{t>s}\sum(1/r_{ts})\sim\sum_{t>s}\sum(1/r_{ts})>0.$$

If, instead of

$$\Big[\sum_{n}(-1/n!)\Big\{-\sum_{t=1}^{N}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big],$$

$$\Big[\sum_{n}(1/n!)\Big\{\sum_{t=1}^{N}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big]$$

is used in $f_1{}^{A}$ and $f_2{}^{A}$, then $f_1{}^{A}>0$ and $f_2{}^{A}>0$.

In conclusion, we can estimate the upper limit of the expected error by using the following equation[16]:

$$\Delta(\mathcal{H}-\lambda)_{RT}=\tfrac{1}{2}(\epsilon_R+\epsilon_T)(\Delta H_{RT}{}^{+}+\Delta H_{RT}{}^{-}),\tag{5.14}$$

where

$$\begin{aligned}\Delta H_{RT}{}^{+}=\tfrac{1}{2}(E_R+E_T-2\lambda)\,|\langle R_0|T_0\rangle|&+\tfrac{1}{2}\{|\langle R_0|\mathcal{G}T_0\rangle|+|\langle T_0|\mathcal{G}R_0\rangle|\}\\&+\tfrac{1}{2}\{|\langle R_0|f_1T_0\rangle|+|\langle T_0|f_1R_0\rangle|\}+\tfrac{1}{2}\{|\langle R_0|\mathcal{V}_1T_0\rangle|+|\langle T_0|\mathcal{V}_1R_0\rangle|\}\\&+\tfrac{1}{2}\{|\langle R_0|\mathcal{V}_2T_0\rangle|+|\langle T_0|\mathcal{V}_2R_0\rangle|\},\end{aligned}$$

$$\Delta H_{RT}{}^{-}=\tfrac{1}{2}\{|\langle R_0|f_2T_0\rangle|+|\langle T_0|f_2R_0\rangle|\}+\tfrac{1}{2}\{|\langle R_0|\mathcal{V}_3T_0\rangle|+|\langle T_0|\mathcal{V}_3R_0\rangle|\},$$

$$f_1=f_1{}^{A}+f_1{}^{B},\qquad f_2=f_2{}^{A}+f_2{}^{B}$$

$$f_1{}^{A}\Phi^{A(Q)}(\rho)=\Big|\sum_{t}\epsilon_t{}^{A}-E^{A(Q)}\Big|\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\Big[\sum_{n}(1/n!)\Big\{\sum_{t=1}^{N}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big]{}^{\vartheta}\Psi_{0h}{}^{A},$$

$$f_2{}^{A}\Phi^{A(Q)}(\rho)=\sum_{\mathcal{P}}\sum_{k}\sum_{h}\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\Big[\sum_{n}(1/n!)\Big\{\sum_{i=1}^{N}(\delta_{\mathcal{P}t}-\delta_t)r_t\Big\}^n\Big]\Big\{\sum_{t}V_t{}^{A}-\sum_{t>s}\sum(1/r_{ts})\Big\}\Big]{}^{\vartheta}\Psi_{0h}{}^{A}.$$

Here T_0 and R_0 mean Φ_{T0} and Φ_{R0} obtained by neglecting the second and higher terms of the molecular wave functions (4.4) by putting $c_0=1$ and $c_K=0(K\neq 0)$.

The error $\Delta(\mathcal{H}-\lambda)_{RT}$ depends essentially on the magnitude of ϵ_R and ϵ_T ,which are defined in Eq. (5.1). Although the exact atomic functions $\Phi^{A(Q)}$ or ${}^{\vartheta}\Psi_h{}^{A(Q)}$ are not known, we can estimate the value of ϵ by assuming that the Hylleraas function is accurate enough for the purpose. According to Green et al.,[14] a Hylleraas-type function Φ_{H} for helium is expanded by

$$\Phi_{\mathrm{H}}=\sum_{K}\Phi_K c_K,$$

where the first term $\Phi_0\equiv\Phi_{\mathrm{HF}}$ is a Hartree-Fock function. Values of coefficients c_K are listed in Table I. As Φ_K corresponds to Φ_{K_i} in Eq. (2.13), Eq. (5.1) is written as

$$\int\Big|\sum_{K=1}^{\infty}\sum_{K'=1}^{\infty}\Phi_K{}^{*}\Phi_{K'}c_K{}^{*}c_{K'}-\Phi_{\mathrm{HF}}{}^{*}\Phi_{\mathrm{HF}}(1-c_{\mathrm{HF}}{}^{2})\Big|\,d\tau<\epsilon.$$

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[16] The operators appearing here are all positive, so it is not necessary to take the absolute value of the operators in Eq. (5.7).

TABLE I. Coefficients c_k in the expansion $\Phi_H=\sum_K \Phi_K c_K$.

	H⁻	He	Li⁺
c_0	0.993206	0.997467	0.998806
c_1	0.115067	0.070256	0.048251
c_2	0.016245	0.010387	0.007179
c_3	0.005375	0.003501	0.002426
$\Sigma_i c_i^2$	0.999991	0.999996	0.999998
c_{HF}[a]	0.969074	0.994907	0.998124

[a] Coefficients of the Hartree-Fock functions.

As the first and second terms in the preceding equation compensate each other, it is quite satisfactory to assume that

$$\epsilon=1-c_{HF}^2=0.0102.$$

Although except for He and Li atoms, good approximate functions of atoms have not yet been obtained, it is possible to estimate the order of magnitude of ϵ in the following manner.

The wave function of the Li⁺ ion is given by

$$\Phi(\mathrm{Li}^+)=\sum_K \Phi_K(\mathrm{Li}^+)c_K(\mathrm{Li}^+), \tag{5.15}$$

where

$$c_0(\mathrm{Li}^+)\approx[1-\epsilon(\mathrm{Li}^+)]^{\frac{1}{2}}. \tag{5.16}$$

This is approximately equal to c_0(He) for the He atom. James[17] has shown that the wave function of the Li atom is written as an antisymmetrized product of $\Phi(\mathrm{Li}^+)$ and $2s$ orbital in good approximation, because the correlation between $1s$ and $2s$ electrons is negligibly small. Then the exact wave function of the Li atom is given by

$$\Phi(\mathrm{Li})=\sum_J \Phi_J'(\mathrm{Li})c_J'(\mathrm{Li}), \tag{5.17}$$

where

$$\Phi_0'(\mathrm{Li})=\sum_{\mathcal{P}} \varepsilon_{\mathcal{P}}\mathcal{P}\Phi(1s^2;\mathrm{Li}^+)\Phi(2s;\mathrm{Li}),$$

and

$$c_0'(\mathrm{Li})=[1-2\epsilon(2s;\mathrm{Li})]^{\frac{1}{2}}, \qquad 2\epsilon(2s;\mathrm{Li})\ll\epsilon(\mathrm{Li}^+). \tag{5.18}$$

The wave function Φ(Li) is easily rewritten so that the first term is built up from the Hartree-Fock function Φ_0(Li):

$$\Phi(\mathrm{Li})=\sum_K \Phi_K(\mathrm{Li})c_K(\mathrm{Li}), \tag{5.19}$$

where

$$\Phi_0(\mathrm{Li})=\sum_{\mathcal{P}} \varepsilon_{\mathcal{P}}\mathcal{P}\{a_0\Phi_0(\mathrm{Li}^+)+a\Phi(\mathrm{Li}^+)\}\Phi(2s;\mathrm{Li}),$$

and $\Phi_0(\mathrm{Li}^+)$ is the Hartree-Fock function of the Li⁺ ion. In the Li atom, the K shell part of the Hartree-Fock function becomes different from $\Phi_0(\mathrm{Li}^+)$ obtained for the Li⁺ ion. The deviation is taken into account by $\Phi(\mathrm{Li}^+)$, which is orthogonal to $\Phi_0(\mathrm{Li}^+)$. James has also shown that

$$a_0=(1-\delta_0^2)^{\frac{1}{2}}, \qquad \delta_0\ll\epsilon(\mathrm{Li}^+). \tag{5.20}$$

The coefficient of the term $\sum_{\mathcal{P}} \varepsilon_{\mathcal{P}}\mathcal{P}\Phi_0(\mathrm{Li}^+)\Phi(2s;\mathrm{Li})$ is therefore $c_0(\mathrm{Li})a_0$. This is also calculated from Eq. (5.17) together with Eq. (5.15), which gives the expression $c_0(\mathrm{Li}^+)c_0'(\mathrm{Li})$. Then we find that

$$c_0(\mathrm{Li})a_0=c_0(\mathrm{Li}^+)c_0'(\mathrm{Li}).$$

By inserting Eqs. (5.16), (5.18), and (5.20) into the preceding equation, it is found that

$$c_0(\mathrm{Li})=\{[1-\epsilon(\mathrm{Li}^+)][1-2\epsilon(2s;\mathrm{Li})]\}^{\frac{1}{2}}/(1-\delta_0)^{\frac{1}{2}}.$$

Then the value of $\epsilon=1-c_0^2(\mathrm{Li})$ for the Li atom is given by

$$\epsilon=1-c_0^2(\mathrm{Li})\approx[\epsilon(\mathrm{Li}^+)+2\epsilon(2s;\mathrm{Li})]/(1-\delta)=\epsilon(\mathrm{Li}^+) \tag{5.21}$$

which is found to be approximately equal to $\epsilon(\mathrm{Li}^+)$ for the Li⁺ ion.

According to the analysis of correlation energy between electrons,[18] every pair of electrons has a constant amount of correlation energy, irrespective of whether the pair appears in free atoms or in ions. The value depends on the symmetry of the electrons. For instance, the correlation energy between two $1s$ orbitals is about 1.5 ev, regardless of whether the pair is included in H⁻, He, Li⁺, Li, Be⁺⁺, Be⁺, or Be. The correlation energy between $1s$ and $2s$ orbitals is always negligible, but two $2s$ orbitals have a correlation energy of about 1 ev. Two $2p$ orbitals have a negligibly small correlation energy if the pair is in triplet state, but the amount will be about 1.5 ev if it is in ^1D state and so on.

The wave function $\Phi(ij)$ of the pair of electrons i and j is written as

$$\Phi(ij)=\Phi_0(ij)c_0(ij)+\Phi_\epsilon(ij)c_\epsilon(ij), \tag{5.22}$$

where

$$\Phi_\epsilon(ij)c_\epsilon(ij)\equiv\sum_K \Phi_K(ij)c_K(ij),$$

and $\Phi_0(ij)$ is the Hartree-Fock function of the system, while

$$c_0(ij)=[1-\epsilon(ij)]^{\frac{1}{2}}, \qquad \epsilon(ij)\ll 1. \tag{5.23}$$

In view of the analysis of the correlation energy, we assume that the ratio $c_0(ij)/c_\epsilon(ij)$ is invariant, irrespective of whether $\Phi(ij)$ is in atoms or in ions, although $\Phi(ij)$ itself may be changed due to distortion of the charge distribution.

The wave function of a three-electron system is therefore expressed as

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[17] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

[18] T. Arai and T. Onishi, J. Chem. Phys. **26**, 70 (1957).

$$\Phi(123)=N\sum_{\mathcal{P}}\varepsilon\mathcal{P}[\Phi_0(123)+\Phi_\epsilon(12)\Phi(3)c_\epsilon(12;3)$$
$$+\Phi_\epsilon(23)\Phi(1)c_\epsilon(23;1)+\Phi_\epsilon(31)\Phi(2)c_\epsilon(31;2)$$
$$+\Phi_\epsilon(123)c_\epsilon(123)],$$

where $\Phi_\epsilon(12)$, $\Phi_\epsilon(23)$, and $\Phi_\epsilon(31)$ are defined by Eq. (5.22) and take the correlation between two electrons into account, whereas $\Phi_\epsilon(123)$ takes care of correlation of higher order. As assumed, the ratio between the Hartree-Fock function $\Phi_0(123)$ and $\Phi_\epsilon(12)\Phi(3)$ in $\Phi(123)$ is given by the coefficients in Eq. (5.22), such that

$$c_\epsilon(12;3)=c_\epsilon(12)/c_0(12).$$

Likewise

$$c_\epsilon(23;1)=c_\epsilon(23)/c_0(23),$$
$$c_\epsilon(31;2)=c_\epsilon(31)/c_0(31).$$

The absolute values of these ratios are small as compared with 1. By neglecting the higher terms including $c_\epsilon(123)$ therefore, $\Phi(123)$ is normalized as follows:

$$\Phi(123)=\sum_{\mathcal{P}}\varepsilon\mathcal{P}[\Phi_0(123)c_0(123)$$
$$+\Phi_\epsilon(12)\Phi(3)c_\epsilon{}^0(12,3)+\Phi_\epsilon(23)\Phi(1)c_\epsilon{}^0(23;1)$$
$$+\Phi_\epsilon(31)\Phi(2)c_\epsilon{}^0(31;2)], \quad (5.24)$$

where

$$c_0(123)=c_0(12)c_0(23)c_0(13),$$
$$c_\epsilon(12;3)=c_\epsilon(12)c_0(23)c_0(13),$$
$$c_\epsilon(23;1)=c_0(12)c_\epsilon(23)c_0(13),$$
$$c_\epsilon(31;2)=c_0(12)c_0(23)c_\epsilon(13). \quad (5.25)$$

By using Eq. (5.23), $c_0(123)=(1-\epsilon_3)^{\frac{1}{2}}$ is rewritten as

$$1-\epsilon_3=[1-\epsilon(12)][1-\epsilon(23)][1-\epsilon(31)],$$

or simply

$$\epsilon_3=\epsilon(12)+\epsilon(23)+\epsilon(31) \quad (5.26)$$

by neglecting the higher terms again.

In general, $c_0(1, 2, \cdots N)$ and ϵ_N are obtained by

$$c_0(12\cdots N)=\prod_{i<j}c_0(ij), \quad (5.27)$$

$$\epsilon_N=\sum_{i<j}\epsilon(ij). \quad (5.28)$$

In the case of a Li atom, the predominant correlation between 1*s* electrons 1 and 2 is represented by $\epsilon(\mathrm{Li}^+)=\epsilon(12)\gg\epsilon(23)$ or $\epsilon(31)$ so that Eq. (5.26) is written as Eq. (5.21), where $\delta\ll1$ is equivalent to the assumption concerning the invariance of correlation energy mentioned previously. The error expected in the calculation of the Li_2 molecule by using the present approximation is shown in Table II.

TABLE II. The error $\Delta(\mathcal{H}-\lambda)_{RT}$ expected in the calculation of Li_2 (ev).

R[a] T	0 0	0 1	1 1
$\frac{1}{2}(E_R+E_T-2\lambda)\langle R_0\mid T_0\rangle$	1.27	1.49	2.14
$\frac{1}{2}\{\langle R_0\mid \mathcal{G}T_0\rangle+\langle T_0\mid \mathcal{G}R_0\rangle\}$	0.02	0.23	0.84
$\frac{1}{2}\{R_0\mid f_1T_0\rangle+\langle T_0\mid f_1R_0\rangle\}$	1.22	6.39	12.78
$\frac{1}{2}\{\langle R_0\mid \mathcal{V}_1T_0\rangle+\langle T_0\mid \mathcal{V}_1R_0\rangle\}$	8.15	7.11	8.15
$\frac{1}{2}\{\langle R_0\mid \mathcal{V}_2T_0\rangle+\langle T_0\mid \mathcal{V}_2R_0\rangle\}$	6.72	3.35	0.00
$\Delta H_{RT}{}^+$	17.38	18.57	23.91
$\frac{1}{2}\{\langle R_0\mid f_2T_0\rangle+\langle T_0\mid f_2R_0\rangle\}$	1.22	6.39	12.78
$\frac{1}{2}\{\langle R_0\mid \mathcal{V}_3T_0\rangle+\langle T_0\mid \mathcal{V}_3R_0\rangle\}$	14.86	14.00	14.86
$\Delta H_{RT}{}^-$	16.08	20.39	27.64
$\frac{1}{2}(\epsilon_R+\epsilon_T)$	0.0038	0.0057	0.0076
$\Delta(\mathcal{H}-\lambda)_{RT}$	0.13	0.22	0.39

[a] $R=0$ or $T=0$ means the lowest covalent structure Li+Li. $R=1$ or $T=1$ means the lowest ionic structure $\mathrm{Li}^++\mathrm{Li}^-$.

6. FURTHER SIMPLIFICATION AND VARIOUS METHODS OF ATOMS IN MOLECULES

We have proposed to construct wave functions in molecules (3.8) from modified atomic wave functions (3.7) so that changes in the charge distribution of atoms in molecules are taken into account. Then the energy matrix is correctly calculated by using Eqs. (4.5) or (4.6). Although exact eigenfunctions of atoms are not available and, even if they are available, would be extremely difficult to use for calculating the energy matrix, we can expand them into series of terms and then each part of the energy matrix (4.6) is evaluated up to a certain decimal point correctly. This is necessary in order to assure the accuracy of the approximation in the calculation of the energy matrix.

A. Method of Deformed Atoms in Molecules[6]

As a first-order approximation, we suggested that the series expansion of the wave function (4.4) be cut off after the first term and that the higher terms be neglected for the calculation of each part of the energy matrix (4.6) except E_T+E_R. Then

$$\langle R\mid \mathcal{H}-\lambda\mid T\rangle_{\mathrm{av\ approx}}=\tfrac{1}{2}(E_R+E_T-2\lambda)\langle R_0\mid T_0\rangle$$
$$+\tfrac{1}{2}\{\langle R_0\mid \mathcal{G}T_0\rangle+\langle T_0\mid \mathcal{G}R_0\rangle\}$$
$$+\tfrac{1}{2}\{\langle R_0\mid \mathcal{F}T_0\rangle+\langle T_0\mid \mathcal{F}R_0\rangle\}$$
$$+\tfrac{1}{2}\{\langle R_0\mid \mathcal{V}T_0\rangle+\langle T_0\mid \mathcal{V}R_0\rangle\}, \quad (6.1)$$

where E_T and E_R are calculated exactly, as given in Eq. (4.5). The upper limit of the possible error is estimated by Eq. (5.14). Wave functions R_0 and T_0 appearing here are equivalent to those in the orbital approach so that there are no difficulties to evaluate the matrix (6.1). Values of atomic energies E_T and E_R are obtained from spectroscopic data more accurately than we can expect from the numerical calculation.

Equation (6.1) is the basic formula of the method of deformed atoms in molecules. We have discussed the physical meaning of the approximation used here and shown the accuracy of the calculation.

B. Use of the Hylleraas-Type Functions

If we start from the Hylleraas-Kinoshita functions to construct atomic functions [case (I)], the convergency of the expansion (4.4) becomes much faster and it is possible to calculate the energy matrix more accurately. This has been done by Pauncz[4] in the calculation of the ground state of H_2. Two structures, covalent Φ_1 and ionic Φ_2, are considered for building up the molecular wave function

$$\Phi=\Phi_1c_1+\Phi_2c_2, \tag{6.2}$$

where

$$\Phi_1=2^{-\frac{1}{2}}\{\Phi^A(1;\mathrm{H})\Phi^B(2;\mathrm{H})+\Phi^B(1;\mathrm{H})\Phi^A(2;\mathrm{H})\}$$

$$\Phi_2=2^{-\frac{1}{2}}\{\Phi^A(12;\mathrm{H}^-)+\Phi^B(12;\mathrm{H}^-)\}.$$

He assumed that $\rho\equiv 1$; then $\mathcal{G}=\mathcal{F}=0$. The interatomic interaction has been calculated by using 3 terms of the Hylleraas function for the H^- ion. The result ($D_e=3.23$ ev) has been compared with the result obtained by applying method (A) ($D_e=3.08$ ev). The agreement is remarkably good.

This calculation has two significant meanings. As the accuracy of the present method (B) is supposed to be satisfactory for calculating energy values (4.6), the agreement obtained herein gives strong support for the accuracy of the approximation proposed in (A).

On the other hand, the results are not so satisfactory as compared with the observed value 4.74 ev. It is difficult to obtain a result much closer to the observed value by adding the higher terms Φ_3, $\Phi_4\cdots$ in Eq. (6.2), because the energy separations between Φ_1, Φ_2 and the higher terms are large and convergency is slow.

By choosing a suitable ρ, we immediately obtain the more reasonable result of 4.58 ev by using the same wave function (6.2). It is therefore very essential to consider the change in charge distribution of atoms in molecules or crystals.

C. Method of Deformed Atoms in Molecules (Conventional Scheme)[6]

Although the method (A) is considerably simpler than (B), it is still difficult to carry out the calculation, because the method is essentially the Heitler-London method and we have nonzero higher permutations, which are not manageable for larger molecules or crystals. Besides, we have unfamiliar terms $\mathcal{G}$ and $\mathcal{F}$ included in the energy matrix (6.1).

In order to eliminate $\mathcal{G}$ and $\mathcal{F}$ and simplify the method, we recall that Eq. (3.14) is valid for any atomic function, because the operator $\mathcal{G}+\mathcal{F}$ takes care of every kind of energy loss due to deficiency of the atomic functions used. The approximate atomic function $\Phi_0^{A(Q)}(\rho)$, made up from orbitals, also satisfies Eq. (3 14). Then it is found that

$$\mathcal{H}^A\Phi_0^{A(Q)}(\rho)=E_0^{A(Q)}\Phi_0^{A(Q)}(\rho)+\mathcal{G}^A\Phi_0^{A(Q)}(\rho)+\mathcal{F}_0^A\Phi_0^{A(Q)}(\rho), \tag{6.3}$$

$$\mathcal{G}^A\Phi_0^{A(Q)}(\rho)=\sum_{\mathcal{P}}\sum_k\sum_h\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\sum_t(-\tfrac{1}{2}\Delta_t\rho^{A(Q)\vartheta}\Psi_k^{A(Q)}-\nabla_t\rho^{A(Q)}\nabla_t{}^{\vartheta}\Psi_k^{A(Q)}),$$

$$\mathcal{F}_0^A\Phi_0^{A(Q)}(\rho)=\sum_{\mathcal{P}}\sum_k\sum_h\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\{\rho^{A(Q)}(\mathcal{H}^A-E_0^{A(Q)})^{\vartheta}\Psi_k^{A(Q)}\},$$

and

$$E_0^{A(Q)}=\int\Phi_0^{A(Q)*}\mathcal{H}^A\Phi_0^{A(Q)}d\tau.$$

If we construct a molecular wave function on the basis of approximate atomic functions instead of exact ones, we find

$$\Phi_{T0}=\Phi_{PQh0}=\sum_{M'}h_{MM'}\sum_{\mathcal{P}_{AB}}\sum_k\bar{U}_{kh}(\mathcal{P}_{AB})\mathcal{P}_{AB}\Phi_0^{A(Q)}(\rho)\Phi_0^{B(P-Q)}(\rho),$$

in place of the one given by Eqs. (3.4) and (4.4). The function Φ_{T0} is the first term that appears in the series expansion (4.4) of the exact molecular function Φ_T. Hereafter we abbreviate Φ_{T0} as T_0. The energy matrix obtained on the basis of T_0 and R_0 is given by

$$\begin{aligned}\langle R_0\mid\mathcal{H}-\lambda\mid T_0\rangle=&\tfrac{1}{2}(E_T{}^0+E_R{}^0-2\lambda)\langle R_0\mid T_0\rangle\\&+\tfrac{1}{2}\{\langle R_0\mid\mathcal{G}T_0\rangle+\langle T_0\mid\mathcal{G}R_0\rangle\}\\&+\tfrac{1}{2}\{\langle R_0\mid\mathcal{F}_0T_0\rangle+\langle T_0\mid\mathcal{F}_0R_0\rangle\}\\&+\tfrac{1}{2}\{\langle R_0\mid\mathcal{V}T_0\rangle+\langle T_0\mid\mathcal{V}R_0\rangle\},\end{aligned}\tag{6.4}$$

where

$$E_T{}^0=E_0^{A(Q)}+E_0^{B(P-Q)},$$

and

$$E_0^{A(Q)}=\langle Q_0^A\mid\mathcal{H}^A\mid Q_0^A\rangle.$$

This formula is obtained in the same way as Eqs. (4.5) and (4.6) have been derived and is mathematically rigorous because of Eq. (6.3). The energy matrix $\langle R\mid\mathcal{H}\mid T\rangle$, obtained on the basis of T and R, made up from correlated atomic functions, is evaluated by using Eq. (6.1) in the first approximation. By comparing Eqs. (6.1) and (6.4), it is found that

$$\langle R\mid\mathcal{H}-\lambda\mid T\rangle_{\text{av approx}}=\langle R_0\mid\mathcal{H}-\lambda\mid T_0\rangle+\tfrac{1}{2}\{(E_T-E_T{}^0)+(E_R-E_R{}^0)\}\langle R_0\mid T_0\rangle, \tag{6.5}$$

if we have the following relation:

$$\begin{aligned}\langle R_0\mid\mathcal{F}T_0\rangle&=\langle R_0\mid\mathcal{F}_0T_0\rangle,\\\langle T_0\mid\mathcal{F}R_0\rangle&=\langle T_0\mid\mathcal{F}_0R_0\rangle.\end{aligned}\tag{6.6}$$

The equation (6.5) had been obtained before (in the method of deformed atoms in molecules)[6] and also by Hurley,[5] the latter rather intuitively (the method of the intra-atomic correlation correction). If the relations (6.6) are correct, Eq. (6.5) is equivalent to—and more convenient than—Eq. (6.1), because the first term $\langle R_0 \mid \mathcal{H}-\lambda \mid T_0\rangle_{\text{av}}$ is equivalent to the energy matrix as it appears in the ordinary orbital approach, and the second term is the correlation energy of atoms in molecules, multiplied by the overlap integral. Both can be evaluated in the same manner as in the orbital approach. Besides, the additional terms $\mathcal{G}$ and $\mathcal{F}$ due to energy loss of atoms in molecules, included in Eq. (6.1), disappear in Eq. (6.5), which makes the method more familiar.

The wave functions Φ_{T0} and Φ_{R0} used here are the Heitler-London functions made up from nonorthogonal orbitals. Then it is not easy to evaluate the matrix $\langle R_0 \mid \mathcal{H} \mid T_0\rangle$, because of the nonvanishing terms in the higher-order permutations. It is possible to transform the Heitler-London functions Φ_{T0} into the molecular orbital functions Φ_{M0} by

$$\Phi_{M0}(\rho)=\sum_T \Phi_{T0}(\rho)\,U_{TM}$$

as long as common orbitals for atoms and ions are used. For simplicity, we use the matrix notation. Then the preceding equation is written as

$$\mathbf{\Phi}_{\text{MO}}{}^0(\rho)=\mathbf{\Phi}_{\text{HL}}{}^0(\rho)\,\mathbf{U} \tag{6.7}$$

by using the row matrices

$$\mathbf{\Phi}_{\text{MO}}{}^0=(\Phi_{M0},\Phi_{N0}\cdots) \qquad \text{and} \qquad \mathbf{\Phi}_{\text{HL}}{}^0=(\Phi_{T0},\,\Phi_{R0}\cdots).$$

The energy matrix (6.5) is written as

$$[\mathbf{H}_{\text{HL}}(\rho)]_{\text{approx}}=\mathbf{H}_{\text{HL}}{}^0(\rho)+\tfrac{1}{2}\{\mathbf{S}(\rho)(\mathbf{E}-\mathbf{E}^0)+(\mathbf{E}-\mathbf{E}^0)\mathbf{S}(\rho)\}, \tag{6.8}$$

where $(\mathbf{E}-\mathbf{E}^0)$ is the diagonal matrix, the elements of which are given by $(E_T-E_T{}^0)\delta_{TR}$. $H_{\text{HL}}{}^0(\rho)$ is the energy matrix $\langle R_0 \mid \mathcal{H} \mid T_0\rangle$ obtained by the Heitler-London functions, whereas $[\mathbf{H}_{\text{HL}}(\rho)]_{\text{approx}}$ is the energy matrix $\langle R \mid \mathcal{H} \mid T\rangle_{\text{av approx}}$ given by the exact functions in the first order of approximation. If we transform our function $\mathbf{\Phi}_{\text{HL}}=(\Phi_T,\Phi_R\cdots)$ to the new function $\mathbf{\Phi}_{\text{MO}}=(\Phi_M,\,\Phi_N\cdots)$ by using the same transformation matrix as in Eq. (6.7), then we find

$$\mathbf{\Phi}_{\text{MO}}(\rho)=\mathbf{\Phi}_{\text{HL}}(\rho)\,\mathbf{U}. \tag{6.9}$$

Here we have to make sure that the functions $\Phi_T(\rho)$, $\Phi_R(\rho)\cdots$ used are made up in such a way that the first terms in the expansion (4.4) are given by $\Phi_{T0}(\rho)$, $\Phi_{R0}(\rho)\cdots$, which are composed of common atomic orbitals for both atoms and ions. Then the energy matrix is given by

$$\begin{aligned}[\mathbf{H}_{\text{MO}}(\rho)]_{\text{approx}}&=\langle\mathbf{\Phi}_{\text{MO}} \mid \mathcal{H} \mid \mathbf{\Phi}_{\text{MO}}\rangle_{\text{av approx}}\\&=\mathbf{U}^\dagger[\mathbf{H}_{\text{HL}}(\rho)]_{\text{approx}}\mathbf{U}\\&=\mathbf{U}^\dagger\mathbf{H}_{\text{HL}}{}^0(\rho)\,\mathbf{U}+\tfrac{1}{2}\mathbf{U}^\dagger\{\mathbf{S}^0(\rho)(\mathbf{E}-\mathbf{E}^0)+(\mathbf{E}-\mathbf{E}^0)\,\mathbf{S}^0(\rho)\}\mathbf{U},\end{aligned}$$

where $\mathbf{U}^\dagger\mathbf{H}_{\text{HL}}{}^0(\rho)\mathbf{U}=\mathbf{H}_{\text{MO}}{}^0(\rho)$ is the energy matrix $\langle\mathbf{\Phi}_{\text{MO}}{}^0 \mid \mathcal{H} \mid \mathbf{\Phi}_{\text{MO}}{}^0\rangle$ in the molecular orbital approach, and $\mathbf{U}^\dagger\mathbf{S}\mathbf{U}=1$ because of orthogonality of the molecular orbital functions. We abbreviate that as

$$\mathbf{U}^\dagger(\mathbf{E}-\mathbf{E}^0)\,\mathbf{U}=(\mathbf{E}-\mathbf{E}^0)_{\text{MO}}.$$

Then it is found that

$$[\mathbf{H}_{\text{MO}}(\rho)]_{\text{approx}}=\mathbf{H}_{\text{MO}}{}^0(\rho)+\tfrac{1}{2}\{(\mathbf{E}-\mathbf{E}^0)_{\text{MO}}+(\mathbf{E}-\mathbf{E}^0)_{\text{MO}}{}^\dagger\}. \tag{6.10}$$

As in the energy matrix $\mathbf{H}_{\text{MO}}{}^0$ in the molecular orbital approach, higher-order permutations vanish, and this is much easier to calculate than Eq. (6.5).

Equations (6.5) and (6.10) are equivalent to Eq. (6.1) if the condition given by Eq. (6.6) is satisfied, and are then a good approximation for calculating the energy matrix. This is unfortunately not correct in the rigorous sense. For instance, if we assume $\rho=1$, then it is immediately found that

$$\mathcal{F}^A\Phi^{A(Q)}=0$$

because the wave function $\Phi^{A(Q)}(\rho=1)$ is an eigenfunction of $\mathcal{H}^A$. But

$$\mathcal{F}^A\Phi_0{}^{A(Q)}\neq 0.$$

From Eq. (4.6), therefore, it is easily found that $\mathbf{H}_{\text{HL}}$ is a diagonal matrix at infinite internuclear distance $R=\infty$ when $\rho=1$, but $\mathbf{H}_{\text{HL}}{}^0$ is not generally diagonal. As the second term $\tfrac{1}{2}\{\mathbf{S}(\mathbf{E}-\mathbf{E}^0)+(\mathbf{E}-\mathbf{E}^0)\,\mathbf{S}\}$ is diagonal at $R=\infty$, Eq. (6.5) or Eq. (6.8) cannot be correct at $R=\infty$. Although $\Phi_0{}^{A(Q)}$ gives the energy value $E_0{}^{A(Q)}$, it is not an eigenfunction of $\mathcal{H}^A$. Therefore use of Eq. (6.8) or Eq. (6.10) introduces another error of

$$\delta F_{RT}=\tfrac{1}{2}\{\,|\,\langle R_0 \mid \mathcal{F}_0T_0\rangle-\langle R \mid \mathcal{F}T\rangle\,|+|\,\langle T_0 \mid \mathcal{F}_0R_0\rangle-\langle T \mid \mathcal{F}R\rangle\,|\,\}, \tag{6.11}$$

in addition to the error due to use of the first-order approximation, introduced in Eq. (6.1). This error δF is the origin of the apparent contradiction at infinite internuclear distance mentioned previously. There is another way to define the interatomic interaction $\langle R \mid \mathcal{V}T\rangle$. Then we obtain an equation similar to Eq. (6.8), but there the definition of $(\mathbf{E}-\mathbf{E}^0)$ is different from the one which has been given in Eq. (6.4). In this method both $\mathbf{H}_{\text{HL}}$ and $\mathbf{H}_{\text{HL}}{}^0$ are diagonal at infinite internuclear distance and there is no such difficulty. Moffitt has introduced the definition[1] which has been used by several people. Hurley has extended the method to propose the method of the intra-atomic correlation correction.[5] In the latter method, however, there is an ambiguity in the definition of $\langle R \mid \mathcal{V}T\rangle$ which can lead to serious mistakes. We discuss the matter in detail in the following two paragraphs.

We now investigate how we can reduce the error δF as much as possible. When $\rho=1$, $\langle R \mid \mathcal{F}T\rangle=0$, then

$$\delta F_{RT}=\tfrac{1}{2}\{\,|\,\langle R_0 \mid \mathcal{F}_0T_0\rangle\,|+|\,\langle T_0 \mid \mathcal{F}_0R_0\rangle\,|\,\}. \tag{6.11$'$}$$

The first term of δF is then essentially written as

$$\delta F^a = \int \Psi^* (\mathcal{H}^A - E_0^{A(Q)}) \Phi_0^{A(Q)} d\tau$$

by using Eq. (6.3). The Hartree-Fock function $\Phi_0^{A(Q)}$ can be expanded in terms of the exact eigenfunctions $\Phi^{A(P)}$ as follows:

$$\Phi_0^{A(Q)} = \sum_P \Phi^{A(P)} c_P,$$

where $\mathcal{H}^A \Phi^{A(P)} = E^{A(P)} \Phi^{A(P)}$. Then it is found that

$$\delta F^a = \int \Psi^* \sum_P (E^{A(P)} - E_0^{A(Q)}) \Phi^{A(P)} c_P d\tau.$$

For a diagonal term $\Psi = \Phi_0^{A(Q)}$, δF becomes zero, because

$$\int \Phi_0^{A(Q)*} \mathcal{H}^A \Phi_0^{A(Q)} d\tau = E_0^{A(Q)},$$

and

$$\delta F^a(\Psi = \Phi^{A(Q)}) = (E^{A(Q)} - E_0^{A(Q)}) c_Q^2 + \sum_P (E^{A(P)} - E_0^{A(Q)}) c_P^2 = 0,$$

where $c_Q^2 \gg c_P^2$, $P \neq Q$. Here the first and second terms cancel each other. In general, we can expand Ψ as

$$\Psi = \sum_P \Phi^{A(P)} d_P.$$

Then

$$\delta F^a = (E^{A(Q)} - E_0^{A(Q)}) d_Q^* c_Q + \sum_P (E^{A(P)} - E_0^{A(Q)}) d_P^* c_P. \quad (6.12)$$

Here $d_P \neq c_P$, therefore δF^a is in general not zero. But as long as we are considering a few atomic states which are close to each other, for instance ${}^3P$, ${}^1D$, and ${}^1S$ states of a C atom with $(1s)^2(2s)^2(2p)^2$ configuration, then the correlation energy between core electrons is constant and we expect that $d_P \approx c_P$, and $d_Q^2 \gg d_P^2$. However,

$$d_Q \approx \int \Psi^* \Phi_0^{A(Q)} d\tau < 1$$

and then the first and second terms in Eq. (6.12) have opposite signs and the same order of magnitude, but $\delta F \neq 0$. If we choose $\Phi_0^{A(Q)}$ so that $E_0^{A(Q)}$ approaches to $E^{A(Q)}$ and c_P's other than c_Q tend to zero, then δF becomes small. The best function $\Phi_0^{A(Q)}$ in the orbital approach is therefore the Hartree-Fock function. In fact, if we take a function $\Phi_0'^{A(Q)}$ different from the Hartree-Fock $\Phi_0^{A(Q)}$, then

$$|(E^{A(Q)} - E_0^{A(Q)}) c_Q| < |(E^{A(Q)} - E_0'^{A(Q)}) c_Q'|,$$

because $E^{A(Q)} < E_0^{A(Q)} < E_0'^{A(Q)}$, whereas $c_Q'/c_Q \approx 1$. In the second term, the difference $E^{A(P)} - E_0^{A(Q)}$ is fairly large so that $E^{A(P)} - E_0^{A(Q)} \approx E^{A(P)} - E_0'^{A(Q)}$, but the increase of the ratio $c_Q'/c_Q > 1$ is more effective and

$$\sum_P (E^{A(P)} - E_0'^{A(Q)}) c_P' / \sum_P (E^{A(P)} - E_0^{A(Q)}) c_P \approx \sum_P c_P' / \sum_P c_P \approx (1 - c_Q'^2)^{\frac{1}{2}} / (1 - c_Q^2)^{\frac{1}{2}}.$$

In the case of $\rho \neq 1$, δF^a is written as

$$\delta F^a = \int \Psi^* \sum_{\mathcal{P}} \sum_k \sum_h \Theta_k \bar{U}_{kh}(\mathcal{P}) \times [\mathcal{P}\{\rho_h^{A(Q)} (\mathcal{H}^A - E_0^{A(Q)}) {}^{\vartheta}\Psi_{0h}^{A(Q)}\}] d\tau$$

$$= \delta F_1^a - E_0^{A(Q)} \delta F_2^a + \delta F_3^a,$$

where

$$\delta F_1^a = \int \Psi^* \mathfrak{F}_1^A \Phi_0^{A(Q)} d\tau,$$

$$\delta F_2^a = \int \Psi^* \mathfrak{F}_2^A \Phi_0^{A(Q)} d\tau,$$

$$\delta F_3^a = \int \Psi^* \mathfrak{F}_3^A \Phi_0^{A(Q)} d\tau,$$

and

$$\mathfrak{F}_3^A \Phi_0^{A(Q)} = \sum_{\mathcal{P}} \sum_k \sum_h \Theta_k \bar{U}_{kh}(\mathcal{P}) \rho^{A(Q)} \times [\mathcal{P}(\mathcal{H}^A - E_0^{A(Q)}) {}^{\vartheta}\Psi_{0h}^{A(Q)}].$$

The expression is obtained by subtracting the term δF_3^a from δF^a and dividing it into δF_1^a and δF_2^a as in Eq. (4.8). Comparing with Eq. (4.8), it is found that

$$\begin{aligned}\delta F_{RT} = \tfrac{1}{2}\{ & |\langle R_0 | \mathfrak{F}_1 T_0 \rangle - E_{T0} \langle R_0 | \mathfrak{F}_2 T_0 \rangle + \langle R_0 | \mathfrak{F}_3 T_0 \rangle \\ & - \langle R_0 | \mathfrak{F}_1 T_0 \rangle + E_T \langle R_0 | \mathfrak{F}_2 T_0 \rangle | \\ & + | \langle T_0 | \mathfrak{F}_1 R_0 \rangle - E_{R0} \langle T_0 | \mathfrak{F}_2 R_0 \rangle \\ & + \langle T_0 | \mathfrak{F}_3 R_0 \rangle - \langle T_0 | \mathfrak{F}_1 R_0 \rangle + E_R \langle T_0 | \mathfrak{F}_2 R_0 \rangle | \} \\ = \tfrac{1}{2}\{ & | (E_T - E_{T0}) \langle R_0 | \mathfrak{F}_2 T_0 \rangle + \langle R_0 | \mathfrak{F}_3 T_0 \rangle | \\ & + | (E_R - E_{R0}) \langle T_0 | \mathfrak{F}_2 R_0 \rangle + \langle T_0 | \mathfrak{F}_3 R_0 \rangle |.\end{aligned}$$

Then we expect the same order of errors again, because the first term is negligibly small and $\langle R_0 | \mathfrak{F}_3 T_0 \rangle$ is equivalent to $\delta F(\rho = 1)$. It is very important, therefore, to construct the atomic wave function such that its first term is made up from Hartree-Fock functions. The correction term ρ can be added after the exact eigenfunction of atoms is obtained.

D. Method of Atoms in Molecules[1,2]

Moffitt has originally proposed to build up the molecular wave functions from exact eigenfunctions of atoms, and suggested to calculate the interatomic interaction by using approximate functions made up from orbitals. There he assumed that the value of the interatomic interaction is not affected by the inaccuracy of approximate functions used, although such functions are poor for calculating the intra-atomic part.

All equations as given by Moffitt are also obtained from the previous results by setting $\rho=1$. From Eq. (4.5) we find that

$$\langle R\,|\,\mathcal{H}\,|\,T\rangle_{\mathrm{av}}=\tfrac{1}{2}(E_T+E_R)\langle R\,|\,T\rangle + \tfrac{1}{2}\{\langle R\,|\,\mathcal{V}T\rangle+\langle T\,|\,\mathcal{V}R\rangle\}$$

or, by using the matrix notation

$$[\mathbf{H}_{\mathrm{HL}}]=\tfrac{1}{2}(\mathbf{SE}+\mathbf{ES})+\tfrac{1}{2}(\mathbf{V}+\mathbf{V}^{\dagger}). \qquad (6.13)$$

This is an exact result obtained immediately if we build up the molecular wave function from exact eigenfunctions of atoms and let the molecular Hamiltonian operate on it. This matrix is conveniently calculated

$$[\mathbf{H}_{\mathrm{HL}}]_{\mathrm{approx}}=\tfrac{1}{2}(\mathbf{S}^0\mathbf{E}+\mathbf{ES}^0)+\tfrac{1}{2}(\mathbf{V}^0+\mathbf{V}^{0\dagger}) \qquad (6.14)$$

which is equivalent to Eq. (6.1); $\mathbf{S}^0$ and $\mathbf{V}^0$ should be evaluated by using the approximate functions Φ_{T0} made up from Hartree-Fock functions of atoms. Then the expected error in this approximation is smaller than the error in Eq. (6.1), because $\mathcal{G}=\mathcal{F}=0$.

The energy matrix $\mathbf{H}_{\mathrm{HL}}{}^0=\langle R_0\,|\,\mathcal{H}\,|\,T_0\rangle$, calculated by approximate functions Φ_{T0}, is written as Eq. (6.4), because the Hartree-Fock functions $\Phi_0{}^{A(Q)}$ satisfy Eq. (6.3). Unlike in Eqs. (6.13) and (6.14), however, terms including $\mathcal{F}_0$ do not vanish even if we set $\rho=1$. If we assume that

$$\langle R_0\,|\,\mathcal{F}_0T_0\rangle=\langle T_0\,|\,\mathcal{F}_0R_0\rangle=0, \qquad (6.15)$$

which is equivalent to Eq. (6.6), then we obtain

$$\mathbf{H}_{\mathrm{HL}}{}^0=\tfrac{1}{2}(\mathbf{S}^0\mathbf{E}^0+\mathbf{E}^0\mathbf{S}^0)+\tfrac{1}{2}(\mathbf{V}^0+\mathbf{V}^{0\dagger}), \qquad (6.16)$$

where $\mathbf{E}^0$ is defined in Eq. (6.4) and is the sum of the Hartree-Fock energies of atoms.

By comparing Eqs. (6.14) and (6.16), we find that

$$[\mathbf{H}_{\mathrm{HL}}]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^0+\tfrac{1}{2}\{\mathbf{S}^0(\mathbf{E}-\mathbf{E}^0)+(\mathbf{E}-\mathbf{E}^0)\mathbf{S}^0\}, \qquad (6.17)$$

which is equivalent to Eq. (6.5). This equality does not hold in the rigorous sense, because off-diagonal elements in $\mathbf{H}_{\mathrm{HL}}{}^0$ do not vanish at infinite nuclear separation.

From Eq. (4.1′) it is found, in the case of $\rho=1$, that

$$\mathbf{V}=\mathbf{H}_{\mathrm{HL}}-\mathbf{SE}. \qquad (6.18)$$

If we assume that approximation to $\mathbf{V}$ is obtained by calculating $\mathbf{H}_{\mathrm{HL}}$, $\mathbf{E}$, and $\mathbf{S}$ by orbital approach, then we have

$$\mathbf{V}^0=\mathbf{H}_{\mathrm{HL}}{}^0-\mathbf{S}^0\mathbf{E}^0,$$

which is equivalent to Eq. (6.16) and $\mathbf{E}^0$ is again the sum of the Hartree-Fock energies of atoms. As long as we are considering the simple Heitler-London scheme in which molecular wave functions are built up from antisymmetrized products of atomic eigenfunctions, $\mathbf{E}$ is equal to the asymptotic form of $\mathbf{H}_{\mathrm{HL}}$ at infinite nuclear separation. Then

$$\mathbf{V}=\mathbf{H}_{\mathrm{HL}}-\mathbf{S}\mathbf{H}_{\mathrm{HL}}(\infty), \qquad (6.19)$$

where

$$\mathbf{H}_{\mathrm{HL}}(\infty)=\lim_{R\to\infty}\mathbf{H}_{\mathrm{HL}}$$

in which R is the internuclear distance. Approximation to $\mathbf{V}$ is therefore given by

$$\mathbf{V}^0=\mathbf{H}_{\mathrm{HL}}{}^0-\mathbf{S}^0\mathbf{H}_{\mathrm{HL}}{}^0(\infty). \qquad (6.20)$$

Moffitt has defined $\mathbf{V}^0$ as Eq. (6.20) and assumed that $\mathbf{V}^0$ is a good approximation to $\mathbf{V}$ in Eq. (6.13). By replacing $\frac{1}{2}(\mathbf{V}+\mathbf{V}^{\dagger})$ in Eq. (6.13) by $\mathbf{V}^0$ and its transposed complex conjugate, we find that

$$[\mathbf{H}_{\mathrm{HL}}]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^0+\tfrac{1}{2}\{\mathbf{S}^0(\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^0(\infty)) + (\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^0(\infty))\mathbf{S}^0\}. \qquad (6.21)$$

Here the equality holds at infinite nuclear distance $R\to\infty$, because

$$\lim_{R\to\infty}\mathbf{S}^0=1.$$

Eigenvalues $\mathbf{E}$ of atoms and $\mathbf{H}_{\mathrm{HL}}(\infty)$ defined by Eq. (6.19) are equal to each other only if the molecular wave functions are written as Eq. (3.4). When the wave functions $\mathbf{H}_{\mathrm{HL}}$ are transformed by

$$\mathbf{\Phi}_x=\mathbf{\Phi}_{\mathrm{HL}}\mathbf{U}$$

the energy matrix $\mathbf{H}_{\mathrm{HL}}$ given by Eq. (6.13) should be transformed to

$$\begin{aligned}[\mathbf{H}_x]&=\mathbf{U}^{\dagger}[\mathbf{H}_{\mathrm{HL}}]\mathbf{U}\\ &=\tfrac{1}{2}\mathbf{U}^{\dagger}(\mathbf{SE}+\mathbf{ES})\mathbf{U}+\tfrac{1}{2}\mathbf{U}^{\dagger}(\mathbf{V}+\mathbf{V}^{\dagger})\mathbf{U}\\ &=\tfrac{1}{2}(\mathbf{S}_x\mathbf{E}_x+\mathbf{E}_x\mathbf{S}_x)+\tfrac{1}{2}(\mathbf{V}_x+\mathbf{V}_x{}^{\dagger}), \end{aligned}\qquad (6.22)$$

where $\mathbf{E}_x=\mathbf{U}^{\dagger}\mathbf{EU}$, $\mathbf{S}_x=\mathbf{U}^{\dagger}\mathbf{SU}$, and $\mathbf{V}_x=\mathbf{U}^{\dagger}\mathbf{VU}$. In the same approximation as in Eq. (6.20), $\mathbf{V}_x{}^0$ should be

$$\begin{aligned}\mathbf{V}_x{}^0(\mathrm{HL})&=\mathbf{U}^{\dagger}\mathbf{V}^0\mathbf{U}=\mathbf{U}^{\dagger}\mathbf{H}_{\mathrm{HL}}{}^0\mathbf{U}-\mathbf{U}^{\dagger}\mathbf{S}^0\mathbf{H}_{\mathrm{HL}}{}^0(\infty)\mathbf{U}\\ &=\mathbf{H}_x{}^0-\mathbf{S}_x{}^0\mathbf{H}_x{}^0(\mathrm{HL},\infty),\end{aligned}\qquad (6.23)$$

where

$$\mathbf{H}_x{}^0=\mathbf{U}^{\dagger}\mathbf{H}_{\mathrm{HL}}{}^0\mathbf{U},$$

and

$$\mathbf{H}_x{}^0(\mathrm{HL},\infty)=\mathbf{U}^{\dagger}\mathbf{H}_{\mathrm{HL}}{}^0(\infty)\mathbf{U}.$$

Then we have

$$[\mathbf{H}_x(\mathrm{HL})]_{\mathrm{approx}}=\mathbf{H}_x{}^0+\tfrac{1}{2}\{\mathbf{S}_x{}^0(\mathbf{E}-\mathbf{H}^0(\mathrm{HL},\infty)) + (\mathbf{E}-\mathbf{H}_x{}^0(\mathrm{HL},\infty))\mathbf{S}_x{}^0\}, \qquad (6.24)$$

which is similar to Eq. (6.21). If we apply the definition (6.20) to calculate $\mathbf{V}_x$ and $\mathbf{V}_x{}^{\dagger}$ in Eq. (6.22) approximately,

$$\mathbf{V}_x{}^0=\mathbf{H}_x{}^0-\mathbf{S}_x{}^0\mathbf{H}_x{}^0(\infty), \qquad (6.25)$$

where

$$\mathbf{H}_x{}^0(\infty)=\lim_{R\to\infty}\mathbf{H}_x{}^0,$$

then we find

$$[\mathbf{H}_x]_{\text{approx}}=\mathbf{H}_x{}^0+\tfrac{1}{2}\{\mathbf{S}^0(\mathbf{E}-\mathbf{H}_x{}^0(\infty))+(\mathbf{E}-\mathbf{H}_x{}^0(\infty))\mathbf{S}^0\}. \quad (6.26)$$

Although this formula is exactly the same as Eq. (6.24) in form, $\mathbf{H}_x$ from Eq. (6.26) is not equal to $[\mathbf{H}_x(\text{HL})]_{\text{approx}}$ given by Eq. (6.24), because $\mathbf{H}_x{}^0(\infty)$ as defined in Eq. (6.25) is not always equal to $\mathbf{H}_x{}^0(\text{HL}, \infty)$ as defined in Eq. (6.23).

For example, we consider the wave function of HeH, made up from the following two terms:

$$\Phi_1=\sum_{\wp}\boldsymbol{\varepsilon}\wp\Phi^{\text{H}}(1)\Phi_1{}^{\text{He}}(23),$$

$$\Phi_2=\sum_{\wp}\boldsymbol{\varepsilon}\wp\Phi^{\text{H}}(1)\Phi_2{}^{\text{He}}(23), \quad (6.27)$$

where Φ^{H} is the wave function of the H atom and $\Phi_1{}^{\text{He}}$ and $\Phi_2{}^{\text{He}}$ are the wave functions of the He atom with configurations $1s)^2\ {}^1S$ and $1s)\ 2s)\ {}^1S$. Then we find that

$$\mathbf{E}=\begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \qquad \mathbf{E}^0=\begin{pmatrix} E_1{}^0 & 0 \\ 0 & E_2{}^0 \end{pmatrix},$$

and

$$\mathbf{H}_{\text{HL}}{}^0(\infty)=\begin{pmatrix} E_1{}^0 & \Delta E \\ \Delta E & E_2{}^0 \end{pmatrix},$$

where

$$E_1=E(\text{H})+E_1(\text{He}), \qquad E_2=E(\text{H})+E_2(\text{He}),$$

$$E_1{}^0=E(\text{H})+E_1{}^0(\text{He}), \qquad E_2{}^0=E(\text{H})+E_2{}^0(\text{He}),$$

$$\Delta E=\int\Phi_{10}{}^{\text{He}*}\mathcal{H}\Phi_{20}{}^{\text{He}}d\tau\neq 0$$

and $E(\text{H})$ is the energy of the H atom and $E_1(\text{He})$ and $E_2(\text{He})$ are energies of the He atom in the $1s)^2\ {}^1S$ and $1s)\ 2s)\ {}^1S$ states, respectively. Because of $\Delta E\neq 0$, it is clearly seen that Eq. (6.17) is not valid at infinite separation, but Eq. (6.21) does not have such a apparent contradiction.

If, instead of Φ_1 and Φ_2, we use the functions Φ_1' and Φ_2',

$$\Phi_1'=\sum_{\wp}\boldsymbol{\varepsilon}\wp\Phi(1)^{\text{H}}\{(1+S^2)^{-\frac{1}{2}}\Phi_1{}^{\text{He}}(23)+[S/(1+S^2)^{\frac{1}{2}}]\Phi_2{}^{\text{He}}(23)\},$$

$$\Phi_2'=\sum_{\wp}\boldsymbol{\varepsilon}\wp\Phi^{\text{H}}(1)\{[-S/(1+S^2)^{\frac{1}{2}}]\Phi_1{}^{\text{He}}(23)+(1+S^2)^{-\frac{1}{2}}\Phi_2{}^{\text{He}}(23)\},$$

which are obtained by linear transformation $\mathbf{U}$ from Φ_1 and Φ_2,

$$\mathbf{U}=(1+S^2)^{-\frac{1}{2}}\begin{pmatrix} 1 & -S \\ S & 1 \end{pmatrix}, \quad \text{where } \lim_{R\to\infty} S=0,$$

then we should expect exactly the same result as before. This is true if we apply the definition in Eq. (6.23). Then we have

$$\mathbf{H}_x{}^0(\text{HL}, \infty)=\mathbf{U}^\dagger\mathbf{H}_{\text{HL}}{}^0(\infty)\mathbf{U}=\begin{pmatrix} \dfrac{E_1{}^0+E_2{}^0S^2+2S\Delta E}{1+S^2}, & \dfrac{(E_2{}^0-E_1{}^0)S+(1-S^2)\Delta E}{1+S^2} \\[2ex] \dfrac{(E_2{}^0-E_1{}^0)S+(1-S^2)\Delta E}{1+S^2}, & \dfrac{E_2{}^0+E_1{}^0S^2-2S\Delta E}{1+S^2} \end{pmatrix},$$

and find that

$$0=|\,[\mathbf{H}_x(\text{HL})]_{\text{approx}}-\lambda\mathbf{S}_x{}^0\,|=\mathbf{U}^\dagger\,|\,[\mathbf{H}_{\text{HL}}]_{\text{approx}}-\lambda\mathbf{S}_{\text{HL}}{}^0\,|\,\mathbf{U}. \quad (6.28)$$

This proves the invariance of the solution.

According to the definition in Eq. (6.25) however,

$$\mathbf{H}_x{}^0(\infty)=\lim_{R\to\infty}\mathbf{H}_x{}^0=\begin{pmatrix} E_1, & \Delta E \\ \Delta E, & E_2 \end{pmatrix},$$

which is different from $\mathbf{H}_x{}^0(\text{HL}, \infty)$; then $[\mathbf{H}_x]_{\text{approx}}$ given by Eq. (6.26) is different from $[\mathbf{H}_x(\text{HL})]_{\text{approx}}$ and does not satisfy Eq. (6.28). Therefore the definition in Eq. (6.25) cannot provide unique solutions of the Schrödinger equation, but the results depend on the choice of the transformation matrix $\mathbf{U}$; which is not correct. Equation (6.19) can be reasonable only if the molecular wave function is built up from simple products of atomic functions as in Eq. (6.27).

Discussion of Eqs. (6.11) and (6.11′) indicates that Eq. (6.16) should be written more exactly as

$$\mathbf{H}_{\text{HL}}{}^0=\tfrac{1}{2}(\mathbf{S}^0\mathbf{E}^0+\mathbf{E}^0\mathbf{S}^0)+\tfrac{1}{2}(\mathbf{V}^0+\mathbf{V}^{0\dagger})+\delta\mathbf{F}.$$

At infinite internuclear separation, this is

$$\mathbf{H}_{\text{HL}}{}^0(\infty)=\mathbf{E}^0+\delta\mathbf{F}(\infty),$$

where

$$\delta\mathbf{F}(\infty)_{RT}=\lim_{R\to\infty}\delta\mathbf{F}_{RT}=\lim_{R\to\infty}\langle R_0\,|\,\mathfrak{F}_0T_0\rangle=\lim_{R\to\infty}\langle T_0\,|\,\mathfrak{F}_0R_0\rangle$$

and

$$\lim_{R\to\infty}\mathbf{S}^0=1;\ \lim_{R\to\infty}\mathbf{V}^0=0$$

Then it is found that

$$\mathbf{H}_{\mathrm{HL}}{}^{0}=\tfrac{1}{2}(\mathbf{S}^{0}\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty)+\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty)\mathbf{S}^{0})+\tfrac{1}{2}(\mathbf{V}^{0}+\mathbf{V}^{0\dagger})$$
$$+\delta\mathbf{F}-\tfrac{1}{2}(\mathbf{S}^{0}\delta\mathbf{F}(\infty)+\delta\mathbf{F}(\infty)\mathbf{S}^{0}).$$

Instead of Eq. (6.8), therefore, we obtain

$$[\mathbf{H}_{\mathrm{HL}}]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^{0}$$
$$+\tfrac{1}{2}\{\mathbf{S}^{0}(\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty))+(\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty))\mathbf{S}^{0}\}$$
$$+\tfrac{1}{2}(\mathbf{S}^{0}\delta\mathbf{F}(\infty)+\delta\mathbf{F}(\infty)\mathbf{S}^{0})-\delta\mathbf{F}. \quad (6.29)$$

This equation is equivalent to Eq. (6.14) and

$$\lim_{R\to\infty}\tfrac{1}{2}(\mathbf{S}^{0}\delta\mathbf{F}(\infty)+\delta\mathbf{F}(\infty)\mathbf{S}^{0})-\delta\mathbf{F}=0.$$

The nonzero value of $\delta\mathbf{F}$ stems from the fact that the Hartree-Fock function Φ_0 does not satisfy the Schrödinger equation $\mathcal{H}\Phi_0=E_0\Phi_0$, but satisfies Eq. (6.3), in which $\mathcal{G}^{A}\Phi_0{}^{A(Q)}=0$ and $\mathcal{F}^{A}\Phi_0{}^{A(Q)}\neq 0$. Therefore $\tfrac{1}{2}(\mathbf{S}^{0}\delta\mathbf{F}(\infty)+\delta\mathbf{F}(\infty)\mathbf{S}^{0})$ and $\delta\mathbf{F}$ are expected to cancel each other partly in Eq. (6.29), even at $R\neq\infty$. Then we can expect that Eq. (6.19) is better than Eq. (6.16). As long as we are considering molecular wave functions made up from atomic functions with different symmetry, however, Eq. (6.19) is equivalent to Eq. (6.16), and

$$\lim_{R\to\infty}\mathbf{H}_{\mathrm{HL}}{}^{0}$$

is diagonal, because there is no interaction between atomic functions with different symmetry. Still there exists the uncertainty in $\mathbf{H}_{x}{}^{0}(\infty)$, however, and Eq. (6.26) is not correct.

As an example, we consider the H_2 molecule. Wave functions Φ_1 and Φ_2 of the covalent and ionic structures are given by

$$\Phi_1=(2+2S_1{}^2)^{-\frac{1}{2}}[\Phi^{A}(1)\Phi^{B}(2)+\Phi^{B}(1)\Phi^{A}(2)], \quad (6.30)$$
$$\Phi_2=(2+2S_2{}^2)^{-\frac{1}{2}}[\Phi^{A}(12)+\Phi^{B}(12)],$$

where

$$S_1=\int\Phi^{A*}(1)\Phi^{B}(1)d\tau,$$

and

$$S_2{}^2=\int\Phi^{A*}(12)\Phi^{B}(12)d\tau.$$

Then

$$\mathbf{E}=\begin{pmatrix}2E_1 & 0\\ 0 & E_2\end{pmatrix},$$

and

$$\mathbf{E}^{0}=\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty)=\begin{pmatrix}2E_1{}^{0} & 0\\ 0 & E_2{}^{0}\end{pmatrix},$$

where

$$E_1=\int\Phi^{A*}(1)\mathcal{H}^{A}(1)\Phi^{A}(1)d\tau,$$

and

$$E_2=\int\Phi^{A}(12)^{*}\mathcal{H}^{A}(12)\Phi^{A}(12)d\tau.$$

We can transform the set to

$$\Phi_1{}'=[\sqrt{2}(1+S_1{}')]^{-1}[(1+S_1{}^2)^{\frac{1}{2}}\Phi_1+(1+S_2{}^2)^{\frac{1}{2}}\Phi_2],$$
$$\Phi_2{}'=[\sqrt{2}(1-S_2{}')]^{-1}[-(1+S_1{}^2)^{\frac{1}{2}}\Phi_1+(1+S_2{}^2)^{\frac{1}{2}}\Phi_2],$$

by the transformation matrix U:

$$\mathbf{U}=\begin{pmatrix}\dfrac{(1+S_1{}^2)^{\frac{1}{2}}}{\sqrt{2}(1+S_1{}')}, & -\dfrac{(1+S_1{}^2)^{\frac{1}{2}}}{\sqrt{2}(1-S_2{}')}\\[2ex] \dfrac{(1+S_2{}^2)^{\frac{1}{2}}}{\sqrt{2}(1+S_1{}')}, & \dfrac{1+S_2{}^2}{\sqrt{2}(1-S_2{}')}\end{pmatrix},$$

where $S_1{}'$ and $S_2{}'$ are normalization constants. If we approximate $\Phi^{A}(12)$ by

$$\Phi^{A}(12)\approx\Phi^{A}(1)\Phi^{A}(2), \quad (6.31)$$

by using the same orbitals used in Φ_1, then

$$S=S_1{}^{0}=S_2{}^{0}=S_1{}'^{0}=S_2{}'^{0},$$

and $\Phi_{10}{}'$ and $\Phi_{20}{}'$ become the molecular orbital functions:

$$\Phi_1{}'\sim\Phi_{10}{}'=[\sqrt{2}(1+S)]^{-1}(\Phi^{A}(1)+\Phi^{B}(1))$$
$$\times(\Phi^{A}(2)+\Phi^{B}(2)),$$
$$\Phi_2{}'\sim\Phi_{20}{}'=[\sqrt{2}(1-S)]^{-1}(\Phi^{A}(1)-\Phi^{B}(1))$$
$$\times(\Phi^{A}(2)-\Phi^{B}(2).$$

However, we find that

$$\mathbf{H}_{\mathrm{MO}}{}^{0}(\mathrm{HL},\infty)=\mathbf{U}^{\dagger}\mathbf{H}_{\mathrm{HL}}{}^{0}(\infty)\mathbf{U}=\begin{pmatrix}\dfrac{1+S^2}{2(1+S)^2}(2E_1+E_2), & \dfrac{1+S^2}{2(1-S^2)}(-2E_1+E_2)\\[2ex] \dfrac{1+S^2}{2(1-S^2)}(-2E_1+E_2), & \dfrac{1+S^2}{2(1-S)^2}(2E_1+E_2)\end{pmatrix},$$

$$\mathbf{H}_{\mathrm{MO}}{}^{0}(\infty)=\lim_{R\to 0}\mathbf{H}_{\mathrm{MO}}{}^{0}=\begin{pmatrix}\tfrac{1}{2}(2E_1+E_2), & \tfrac{1}{2}(-2E_1+E_2)\\ \tfrac{1}{2}(-2E_1+E_2), & \tfrac{1}{2}(2E_1+E_2)\end{pmatrix},$$

and $\mathbf{H}_{\mathrm{MO}}{}^{0}(\mathrm{HL},\infty)\neq\mathbf{H}_{\mathrm{MO}}{}^{0}(\infty)$.

If we begin with the molecular orbital functions and want to apply Eq. (6.21), at first we evaluate $\mathbf{H}_{\mathrm{MO}}{}^0$ and transform it to $\mathbf{H}_{\mathrm{HL}}{}^0$ by

$$\mathbf{H}_{\mathrm{HL}}{}^0=\mathbf{U}^{-1\dagger}\mathbf{H}_{\mathrm{MO}}{}^0\mathbf{U}^{-1},$$

where

$$\mathbf{U}^{-1}=\begin{pmatrix} \dfrac{1+S}{\sqrt{2}(1+S^2)^{\frac{1}{2}}} & \dfrac{1+S}{\sqrt{2}(1+S^2)^{\frac{1}{2}}} \\ -\dfrac{1-S}{\sqrt{2}(1+S^2)^{\frac{1}{2}}} & \dfrac{1-S}{\sqrt{2}(1+S^2)^{\frac{1}{2}}} \end{pmatrix},$$

and

$$\Phi_1=[\sqrt{2}(1+S^2)^{\frac{1}{2}}]^{-1}\{(1+S)\Phi_1'-(1-S)\Phi_2'\}, \tag{6.32}$$

$$\Phi_2=[\sqrt{2}(1+S^2)^{\frac{1}{2}}]^{-1}\{(1+S)\Phi_1'+(1-S)\Phi_2'\}.$$

Instead we define the functions

$$\Phi_1''=[\sqrt{2}(1+S^2)^{\frac{1}{2}}]^{-1}(\Phi_1'-\Phi_2'),$$

$$\Phi_2''=[\sqrt{2}(1+S^2)^{\frac{1}{2}}]^{-1}(\Phi_1'+\Phi_2'), \tag{6.33}$$

or

$$\mathbf{\Phi}_x''=\mathbf{\Phi}_{\mathrm{MO}}\mathbf{U}'^{-1}$$

and

$$\mathbf{U}'^{-1}=[2(1+S^2)]^{-\frac{1}{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$

Then

$$\mathbf{H}_x{}^0(\mathrm{HL},\infty)=\mathbf{U}'^{-1\dagger}\mathbf{U}^{-1\dagger}\mathbf{H}_{\mathrm{HL}}{}^0(\infty)\mathbf{U}^{-1}\mathbf{U}'^{-1}$$

$$=(1-S^2)^{-2}\cdot\begin{pmatrix} (2E_1+E_2S^2), & -S(2E_1+E_2) \\ -S(2E_1+E_2), & (2E_1S^2+E_2) \end{pmatrix},$$

which is definitely different from

$$\mathbf{H}_{\mathrm{HL}}{}^0(\infty)=\begin{pmatrix} 2E_1, & 0 \\ 0\ , & E_2 \end{pmatrix}.$$

In molecules the overlap integrals S are not small and especially nonzero off-diagonal elements in $\mathbf{H}_x{}^0(\mathrm{HL},\infty)$ are important.

This difference between $\mathbf{H}_{\mathrm{HL}}{}^0(\infty)$ and $\mathbf{H}_x{}^0(\mathrm{HL},\infty)$ is clearly indicated by the results of the calculation on the Li_2 molecule by Rahman[19] and Fieschi.[20] The latter regarded Φ_1'' and Φ_2'' as the Heitler-London function, the former used Eq. (6.17). The calculation of the O_2 molecule by Moffitt[1] is also based on Φ_1'' and Φ_2'' and neglects the difference between U and U'. Therefore it is expected that there exists the same error as in Fieschi's calculation.

In order to transform the Heitler-London scheme to the molecular orbital scheme in Moffitt's method, we assume that the Hartree-Fock orbitals for free atoms are also a good approximation to the Hartree-Fock orbitals for free ions so that common atomic orbitals are available to construct the approximate functions for atoms and ions, as postulated in Eq. (6.31). Several authors[3] have pointed out, however, that the use of common atomic orbitals for atoms and ions produces serious errors. Therefore it is impossible to rewrite Eq. (6.26) in a form similar to Eq. (6.10) in order to apply the equation in the molecular orbital scheme. In the calculations on the Li_2 molecule by Fieschi and on the O_2 molecule by Moffitt, such error was accidentally compensated by the error due to use of the incorrect transformation matrix U' instead of U. Values obtained by them, although satisfactory, cannot have any physical significance.

E. Method of Intra-Atomic Correlation Correction by Hurley[5]

The method is equivalent to the second formula (6.8) or (6.10), and all discussions given in (C) are also applicable to this case. Therefore the results obtained by this method are not empirical but purely theoretical, and are comparable to the results of the traditional orbital approach, although Hurley did not give a theoretical proof for obtaining his formula (6.10), but obtained it rather intuitively.

His discussions are as follows. Moffitt's formula (6.17) or (6.21) gives a reasonable result for the calculation of the H_2 molecule if a Slater orbital $\phi(z)=(z^3/\pi)^{\frac{1}{2}}e^{-zr}$ (where $z=0.6875$) is used for evaluating the ionic terms in $\mathbf{H}_{\mathrm{HL}}{}^0$ and $\mathbf{H}_{\mathrm{HL}}{}^0(\infty)$. The value $z=0.6875$ is obtained by optimizing the energy of the H^- ion and ϕ with this value of z is a good approximation of the Hartree-Fock orbital for the H^- ion. Then $\phi^A(1,z)\phi^A(2,z)$ is a good approximate function of the exact eigenfunction $\Phi_2{}^A(12)$ of the H^- ion. If we assume $z=1$, where the orbital $\phi_{(z=1)}$ is the same as the wave function of a H atom, the energy of the H_2 molecule drops too much. To illustrate this difficulty

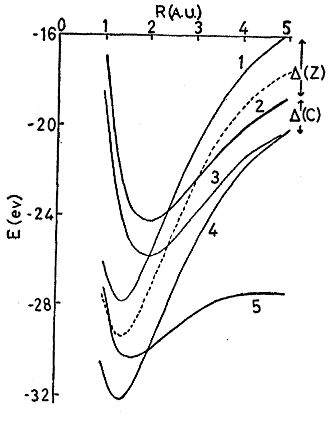

FIG. 2. Calculated energies obtained by various ionic functions of H_2 are illustrated as function of the nuclear separation. Curve 1, $E_2{}^0$ $(z=1)$; curve 2, $E_2{}^0(z=0.6875)$; curve 3, E_2 and $E_2(z0.6875)$; and curve 4, $E_2(z=1)$. Curve 5 gives energy E_1 obtained by covalent wave function, whereas dotted curve indicates energy expected from the ideal ionic function. (Reproduced from the first of references 5 with the permission of the Physical Society of London.)

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[19] A. Rahman, Physica **20**, 623 (1954).

[20] R. Fieschi, Nuovo cimento **6**, 197 (1957).

we show the energy of various ionic wave functions:

$$\Phi_{20}(z=0.6875)$$

$$=[2+2S^0(z)]^{-\frac{1}{2}}[\phi^A(1,z)\phi^A(2,z)+\phi^B(1,z)\phi^B(2,z)],$$

$$\Phi_{20}(Z=1)=(2+2S^0)^{-\frac{1}{2}}[\phi^A(1)\phi^A(2)+\phi^B(1)\phi^B(2)],$$

$$\Phi_2=(2+2S)^{-\frac{1}{2}}[\Phi^A(12)+\Phi^B(12)],$$

in Fig. 2, where $E_2(z=0.6875)$ and $E_2(z=1)$ are obtained by using Eq. (6.21), in which $\Phi_{20}(z=0.6875)$ and $\Phi_{20}(z=1)$ are used for calculating $\mathbf{H}_{\mathrm{HL}}{}^0$ and $\mathbf{H}_{\mathrm{HL}}{}^0(\infty)$, respectively. Since $\Phi_{20}(z=0.6875)$ is a good approximate function of Φ_2, the two functions give nearly the same variation of energy with nuclear separation. Therefore the energy $E_2{}^0(z=0.6875)$ obtained by Φ_{20} is a good approximation to the energy E_2 given by Φ_2. The energy $E_2(z=0.6875)$ is reasonable, but it is evident that $E_2(z=1)$ is a very poor approximation to E_2, giving an error of 8 ev. It is also clear that Φ_2 is not a suitable function for calculating the ground state of the H_2 molecule, because its energy E_2 is considerably higher than the energy $E_2{}^0(z=1)$ given by the simple orbital function $\Phi_{20}(z=1)$.

Hurley assumed then that there exists a function $\Phi_2(z=1)$, which includes correlation between electrons but still its charge distribution is different from one given by the eigenstate Φ_2, although similar to that of $\Phi_{20}(z=1)$. In the present method, modified atomic functions $\Phi(z)$ are used as basics. Then he made the two following statements:

(i) By extending Eq. (6.17), the energy matrix for the modified function $\Phi(z)$ is evaluated by

$$[\mathbf{H}_{\mathrm{HL}}(z)]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^0(z)+\tfrac{1}{2}[\mathbf{S}^0(z)\{\mathbf{E}(z)-\mathbf{E}^0(z)\}+\{\mathbf{E}(z)-\mathbf{E}^0(z)\}\mathbf{S}^0(z)],$$

where

$$\mathbf{H}_{\mathrm{HL}}{}^0(z)=\int\mathbf{\Phi}_0{}^*(z)\mathcal{H}\mathbf{\Phi}_0(z)d\tau,$$

$$\mathbf{E}(z)=\mathbf{E}^A(z)+\mathbf{E}^B(z),$$

$$\mathbf{E}^0(z)=\mathbf{E}^{A0}(z)+\mathbf{E}^{B0}(z),$$

$$\mathbf{E}^A(z)=\int\Phi^{A*}(z)\mathcal{H}^A\Phi^A(z)d\tau,$$

$$\mathbf{E}^{A0}(z)=\int\Phi_0{}^{A*}(z)\mathcal{H}^A\Phi_0{}^A(z)d\tau.$$

(ii) The correlation energy is independent of the value of z; then

$$\mathbf{E}(z)-\mathbf{E}^0(z)=\mathbf{E}-\mathbf{E}^0, \tag{6.34}$$

where $E=E^A+E^B$ is the sum of eigenvalues of free atoms and E^0 is given by the Hartree-Fock functions or evaluated approximately by a Slater orbital with optimum z_0. For the H^- ion, $z=0.6875$. Then the equation is written as

$$[\mathbf{H}_{\mathrm{HL}}(z)]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^0(z)+\tfrac{1}{2}\{\mathbf{S}(\mathbf{E}-\mathbf{E}^0)+(\mathbf{E}-\mathbf{E}^0)\mathbf{S}\}. \tag{6.35}$$

Equation (6.34) is obtained from Eqs. (3.14) and (6.3), that is,

$$E^{A(Q)}(z)=E^{A(Q)}(\rho)=\int\Phi^{A(Q)*}(\rho)\mathcal{H}^A\Phi^{A(Q)}(\rho)d\tau$$

$$=E^{A(Q)}+\langle Q\mid\mathfrak{G}^AQ\rangle+\langle Q\mid\mathfrak{F}^AQ\rangle$$

$$E_0{}^{A(Q)}(z)=E_0{}^{A(Q)}(\rho)=\int\Phi_0{}^{A(Q)*}(\rho)\mathcal{H}^A\Phi_0{}^{A(Q)}(\rho)d\tau$$

$$=E_0{}^{A(Q)}+\langle Q_0\mid\mathfrak{G}^AQ_0\rangle+\langle Q_0\mid\mathfrak{F}_0{}^AQ_0\rangle.$$

In the first order of approximation, the first equation is written as

$$[E^{A(Q)}(z)]_{\mathrm{approx}}=E^{A(Q)}+\langle Q_0\mid\mathfrak{G}^AQ_0\rangle+\langle Q_0\mid\mathfrak{F}^AQ_0\rangle, \tag{6.36}$$

and by assuming $\langle Q_0\mid\mathfrak{F}^AQ_0\rangle=\langle Q_0\mid\mathfrak{F}_0{}^AQ_0\rangle$, it is found that

$$E^{A(Q)}(z)-E_0{}^{A(Q)}(z)\approx E^{A(Q)}-E_0{}^{A(Q)}.$$

In order to eliminate the preceding assumption, we may use

$$[\mathbf{H}_{\mathrm{HL}}(z)]_{\mathrm{approx}}=\mathbf{H}_{\mathrm{HL}}{}^0(z)+\tfrac{1}{2}\{\mathbf{S}^0(z)(\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^0(\infty))+(\mathbf{E}-\mathbf{H}_{\mathrm{HL}}{}^0(\infty))\mathbf{S}^0(z)\}.$$

We have already discussed the difference between $\mathbf{H}_{\mathrm{HL}}{}^0(\infty)$ and E^0. The assumption (6.36) is based on the estimation of error by cutting off higher terms of $\mathfrak{G}$ and $\mathfrak{F}$ integrals, given in Sec. 5.

F. United-Atom Approach Introduced by Bingel and Preuss[21]

So far we have assumed that the interatomic interaction is a small perturbation as compared with the total electronic energy of atoms, and then the molecular wave function, which is exact at infinite internuclear separation, is built up from antisymmetrized products of atomic functions. The effect of interatomic interaction at finite distances is taken into account by the correction term ρ and configuration interaction. The latter takes care of the correlation energy between valence electrons and the correction term includes distortion of the charge cloud due to the existence of neighboring atoms.

It is possible to start from zero internuclear distance, where a molecule may become a united atom. For instance, the two electrons in a H_2 molecule can be treated as if they are in a He atom, considering the effect of finite internuclear distance as a small perturbation. This approach is more artificial than the sepa-

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[21] W. Bingel, Z. Physik **12a**, 59 (1957); H. Preuss, Z. Naturforsch. **12a**, 599 (1957).

rated atom treatment, because ground states and lower excited states of molecules still have the properties of atoms from which the molecules are built up preserved to a considerable extent, whereas molecules show little similarity to united atoms. Perturbation in the separated atom treatment is accordingly smaller than perturbation in the united-atom approach.

Although the starting point is poor, reasonable results for H_2 and CH_4 molecules have been obtained by this method,[22] with orbital functions including configuration interaction. The great advantage of this approach is that the numerical calculation is very much simpler than in the separated atom treatment, although the chemical picture is lost in the wave function. We must realize that we use eigenfunctions of atoms instead of approximate atomic functions; then we can include correlation energy in atoms and remove the difficulty pointed out by Moffitt. This has been carried out by Bingel, whose wave function is made up from eigenfunctions of free atoms; the method corresponds to the original Moffitt method.

In actual calculations in orbital functions, however, it has been shown that the convergency of the configuration interaction is slow, unless we choose suitable basics which are very much different from atomic orbitals in free atoms. That means it is very important to consider the deformation of atoms. Therefore, we use the modified atomic function introduced in Eq. (3.7) as basic of the molecular wave function here. We consider a diatomic molecule AB with N_A+N_B electrons as before. Then our basics are given by

$$\Phi_M{}^U(\rho)=\sum_{\mathcal{P}}\sum_k\sum_h\Theta_k\bar{U}_{kh}(\mathcal{P})\mathcal{P}\,{}^{\vartheta}\Psi_h(\rho),\tag{6.37}$$

which is expanded as

$$\Phi_M{}^U(\rho)=\sum_K\Phi_{MK}{}^U(\rho)\,c_K\tag{6.38}$$

as in Eq. (2.13) or Eq. (4.4). The first term $\Phi_{M0}{}^U(\rho)$ is built up from the primitive function ${}^{\vartheta}\Psi_h$ of the Hartree-Fock function in a free atom, multiplied by a correction term ρ, as is shown in Eq. (3.7). $\Phi_M{}^U(\rho)$ satisfies Eq. (3.14), that is,

$$\mathcal{H}^U\Phi_M{}^U(\rho)=E_M{}^U\Phi_M{}^U(\rho)+\mathcal{G}^U\Phi_M{}^U(\rho)+\mathcal{F}^U\Phi_M{}^U(\rho),\tag{6.39}$$

where

$$\mathcal{H}^U=\sum_{i=1}^{N_A+N_B}\{-(\hbar^2/2m)\nabla_i{}^2+V^U(r_i)\}+\tfrac{1}{2}\sum_{i\neq j}^{N_A+N_B}\sum(e^2/r_{ij});$$

$$V^U(\boldsymbol{r}_i)=(Z_A+Z_B)e^2/r_{U\,i},$$

and $r_{U\,i}$ is the distance between the position of electron i and the center of the united atom U; furthermore, Z_A+Z_B is a sum of nuclear charges Z_A and Z_B, in atoms A and B. $E_M{}^U$ is an eigenvalue of the united atom U in the free state and is given by

$$E_M{}^U=\int\Phi_M{}^{U*}(\rho=1)\mathcal{H}^U\Phi_M{}^U(\rho=1)\,d\tau.$$

The molecular Hamiltonian $\mathcal{H}$ is written as

$$\mathcal{H}=\sum_{i=1}^{N_A+N_B}\{-(\hbar^2/2m)\nabla_i{}^2+V^A(r_i)+V^B(r_i)\}+\tfrac{1}{2}\sum_{i\neq j}^{N_A+N_B}\sum(e^2/r_{ij}),$$

where $V^A(\boldsymbol{r}_i)=Z_Ae^2/r_{A\,i}$, $V^B(r_i)=Z_Be^2/r_{B\,i}$, and $r_{A\,i}$ is the distance between the positions of electron i and nucleus A. The molecular energy matrix H_{NM} is then given by

$$H_{NM}=\langle N\,|\,\mathcal{H}\,|\,M\rangle=\langle N\,|\,\mathcal{H}^U\,|\,M\rangle+\langle N\,|\,\mathcal{V}^U\,|\,M\rangle,\tag{6.40}$$

where the interatomic interaction operator $\mathcal{V}^U$ is defined by

$$\mathcal{V}^U=\mathcal{H}-\mathcal{H}^U=\sum_{i=1}^{N_A+N_B}\{V^A(r_i)+V^B(r_i)-V^U(r_i)\}.$$

By using Eq. (6.39), H_{NM} is written as

$$H_{NM}=E_M{}^U\langle N\,|\,M\rangle+\langle N\,|\,\mathcal{G}^UM\rangle+\langle N\,|\,\mathcal{F}^UM\rangle+\langle N\,|\,\mathcal{V}^U\,|\,M\rangle.\tag{6.41}$$

In order to evaluate H_{NM}, we expand each term by using Eq. (6.38). Basics Φ_{MK} are given analytically; the matrix $\langle N_J\,|\,\mathcal{L}M_K\rangle$ obtained by expansion can be evaluated. As proposed before, we must evaluate E_M accurately, but we may calculate other terms approximately by cutting off the higher terms. Then we have to examine each element in order to retain the Hermitian properties of the appromately obtained energy matrix H_{NM}. Both terms in Eq. (6.40) are Hermitian, but $\langle N\,|\,\mathcal{G}M\rangle$ and $\langle N\,|\,\mathcal{F}M\rangle$ and $E_M\langle N\,|\,M\rangle$ are not. Instead of Eq. (6.41), we should use the following equation:

$$\begin{aligned}[H_{NM}]=\langle N\,|\,\mathcal{H}\,|\,M\rangle_{\text{av}}=&\tfrac{1}{2}(E_M{}^U+E_N{}^U)\langle N\,|\,M\rangle\\&+\tfrac{1}{2}\{\langle N\,|\,\mathcal{G}^UM\rangle+\langle M\,|\,\mathcal{G}^UN\rangle\}\\&+\tfrac{1}{2}\{\langle N\,|\,\mathcal{F}^UM\rangle+\langle M\,|\,\mathcal{F}^UN\rangle\}+\langle N\,|\,\mathcal{V}^U\,|\,M\rangle.\end{aligned}\tag{6.42}$$

By applying the first order of approximation mentioned in (A), we obtain

$$\begin{aligned}\langle N\,|\,\mathcal{H}-\lambda\,|\,M\rangle_{\text{av approx}}=&\tfrac{1}{2}(E_M{}^U+E_N{}^U-2\lambda)\langle N_0\,|\,M_0\rangle\\&+\tfrac{1}{2}\{\langle N_0\,|\,\mathcal{G}^UM_0\rangle+\langle M_0\,|\,\mathcal{G}^UN_0\rangle\}\\&+\tfrac{1}{2}\{\langle N_0\,|\,\mathcal{F}^UM_0\rangle+\langle M_0\,|\,\mathcal{F}^UN_0\rangle\}+\langle N_0\,|\,\mathcal{V}^U\,|\,M_0\rangle.\end{aligned}\tag{6.43}$$

This is equivalent to Eq. (6.1).

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[22] T. C. Chen, J. Chem. Phys. **29**, 356 (1958); H. W. Joy and R. G. Parr, ibid. **28** 448 (1958); S. Hagstrom and H. Shull, ibid. **30**, 1314 (1958); S. Koide et al., J. Phys. Soc. Japan **12**, 1016 (1957); L. M. Mills, J. Mol. Phys. **1**, 99 (1958).

The first term $\Phi_{T0}(\rho)$ in the expansion (6.38) satisfies the equation

$$\mathcal{H}^U\Phi_{M0}{}^U(\rho)=E_{M0}{}^U\Phi_{M0}{}^U(\rho)+\mathcal{G}^U\Phi_{M0}{}^U(\rho)+\mathcal{F}_0{}^U\Phi_{M0}{}^U(\rho),$$

where $\mathcal{F}_0{}^U$ is similar to $\mathcal{F}_0{}^A$ in Eq. (6.3). Then the energy matrix on the basics $\Phi_{M0}{}^U(\rho)$ and $\Phi_{N0}{}^U(\rho)$ is given by

$$\begin{aligned}\langle N_0\,|\mathcal{H}-\lambda\,|\,M_0\rangle_{\text{av approx}}=&\tfrac{1}{2}(E_{M0}{}^U+E_{N0}{}^U-2\lambda)\,\langle N_0|\,M_0\rangle\\&+\tfrac{1}{2}\{\langle N_0\,|\,\mathcal{G}^UM_0\rangle+\langle M_0\,|\,\mathcal{G}^UN_0\rangle\}\\&+\tfrac{1}{2}\{\langle N_0\,|\,\mathcal{F}_0{}^UM_0\rangle+\langle M_0\,|\,\mathcal{F}_0{}^UN_0\rangle\}\\&+\langle N_0\,|\,\mathcal{V}^U\,|\,M_0\rangle,\end{aligned}$$

where $E_{M0}{}^U=\langle M_0\,|\,\mathcal{H}^U\,|\,M_0\rangle$. Then we obtain the convenient equation

$$\begin{aligned}\langle N\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av approx}}=&\langle N_0\,|\,\mathcal{H}\,|\,M_0\rangle\\&+\tfrac{1}{2}\{(E_M{}^U-E_{M0}{}^U)+(E_N{}^U-E_{N0}{}^U)\}\,\langle N_0\,|\,M_0\rangle,\end{aligned}$$

or

$$\begin{aligned}[\mathbf{H}_U]_{\text{approx}}=&\mathbf{H}_U{}^0\\&+\tfrac{1}{2}\{\mathbf{S}_U{}^0(\mathbf{E}_U-\mathbf{E}_U{}^0)+(\mathbf{E}_U-\mathbf{E}_U{}^0)\,\mathbf{S}_U{}^0\},\end{aligned}\qquad(6.44)$$

which corresponds to Eq. (6.5). This equation is equivalent to Eq. (6.43) if

$$\langle N_0\,|\,\mathcal{F}^UM_0\rangle=\langle N_0\,|\,\mathcal{F}_0{}^UM_0\rangle,$$

$$\langle M_0\,|\,\mathcal{F}^UN_0\rangle=\langle M_0\,|\,\mathcal{F}_0{}^UN_0\rangle.$$

At zero internuclear distance, $[\mathbf{H}_U]$ and $\tfrac{1}{2}[\mathbf{S}_U{}^0(\mathbf{E}_U-\mathbf{E}_U{}^0)+(\mathbf{E}_U-\mathbf{E}_U{}^0)\,\mathbf{S}_U{}^0\}$ become diagonal, but $\mathbf{H}_U{}^0$ is not necessarily diagonal. This is the same difficulty as the one discussed in Eqs. (6.18)–(6.20). In order to eliminate this problem, we may use

$$\begin{aligned}[\mathbf{H}_U]_{\text{approx}}=&\mathbf{H}_U{}^0\\&+\tfrac{1}{2}\{\mathbf{S}_U[\mathbf{E}_U-\mathbf{H}_U{}^0(0)]+(\mathbf{E}_U-\mathbf{H}_U{}^0(0))\,\mathbf{S}_U\},\end{aligned}\qquad(6.45)$$

where

$$\mathbf{H}_U{}^0(0)=\lim_{R\to 0}\mathbf{H}_U{}^0.$$

This formula is correct if the basic is an atomic function given by Eq. (6.37), but is not correct if we include a linear combination of these basics. The discussion about Eqs. (6.17) and (6.21) is also applicable here, and Eqs. (6.44) and (6.45) are equivalent as long as the basics $\Phi_M{}^U$ considered have different symmetry at zero internuclear distance.

The molecular wave function Φ^U thus obtained by the united-atom approach is an exact one if the internuclear separation R becomes zero (where $\rho=1$), but the accuracy of the function is reduced as the distance R becomes finite. On the other hand, the molecular wave function Φ, obtained by the separated-atom scheme, is an exact solution when $R\to\infty$ (where $\rho=1$), but for the finite distance Φ is an approximation and the smaller the distance, the poorer the approximation.

Preuss has suggested use of linear combinations of Φ and Φ^U as a molecular wave function. Then we have

$$\Phi_x=\Phi_{TM}=(p_x+1)^{-1}(p_x\Phi_T+\Phi_M{}^U).$$

Here p_x is a function of R and it is evident that

$$\lim_{R\to 0}p_x(R)=0,\qquad \lim_{R\to\infty}p_x(R)=\infty,$$

giving exact solutions as follows:

$$\lim_{R\to 0}\Phi_x=\Phi_M{}^U(\rho=1),\qquad \lim_{R\to\infty}\Phi_x=\Phi_T(\rho=1).$$

Now the energy matrix is given by

$$\begin{aligned}\langle Y\,|\,\mathcal{H}\,|\,X\,\rangle_{\text{av}}=&[(p_x+1)\,(p_y+1)]^{-1}\\&\times\{p_xp_y\langle R\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}+p_x\langle N\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}\\&+p_y\langle R\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av}}+\langle N\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av}}\},\end{aligned}\qquad(6.46)$$

where $\langle R\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}$ and $\langle N\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av}}$ are given by Eqs. (4.5) and (6.42), respectively. By applying Eqs. (4.1′) and (6.41), $\langle N\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}$ and $\langle R\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av}}$ are given by

$$\langle N\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}=\tfrac{1}{2}\{\langle N\,|\,\mathcal{H}\,|\,T\,\rangle+\langle T\,|\,\mathcal{H}\,|\,N\,\rangle\},\qquad(6.47)$$

where

$$\begin{aligned}\langle N\,|\,\mathcal{H}\,|\,T\,\rangle=&E_T\langle N\,|\,T\,\rangle+\langle N\,|\,\mathcal{G}T\,\rangle\\&+\langle N\,|\,\mathcal{F}T\,\rangle+\langle N\,|\,\mathcal{V}T\,\rangle,\end{aligned}$$

and

$$\begin{aligned}\langle T\,|\,\mathcal{H}\,|\,N\,\rangle=&E_N{}^U\langle T\,|\,N\,\rangle+\langle T\,|\,\mathcal{G}^UN\,\rangle\\&+\langle T\,|\,\mathcal{F}^UN\,\rangle+\langle T\,|\,\mathcal{V}^U\,|\,N\,\rangle.\end{aligned}$$

In the first order of approximation, $\langle R\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av}}$ and $\langle N\,|\,\mathcal{H}\,|\,M\,\rangle_{\text{av}}$ are evaluated by Eqs. (6.1) and (6.43), or Eqs. (6.17) and (6.44). $\langle N\,|\,\mathcal{H}\,|\,T\,\rangle$ and $\langle T\,|\,\mathcal{H}\,|\,N\,\rangle$ are also written as

$$\begin{aligned}\langle N\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{approx}}=&E_T\langle N_0\,|\,T_0\rangle+\langle N_0\,|\,\mathcal{G}T_0\rangle\\&+\langle N_0\,|\,\mathcal{F}T_0\rangle+\langle N_0\,|\,\mathcal{V}T_0\rangle,\end{aligned}\qquad(6.48)$$

and

$$\begin{aligned}\langle T\,|\,\mathcal{H}\,|\,N\,\rangle_{\text{approx}}=&E_N{}^U\langle T_0\,|\,N_0\rangle+\langle T_0\,|\,\mathcal{G}^UN_0\rangle\\&+\langle T_0\,|\,\mathcal{F}^UN_0\rangle+\langle T_0\,|\,\mathcal{V}^U\,|\,N_0\rangle,\end{aligned}$$

or

$$\begin{aligned}\langle N\,|\,\mathcal{H}\,|\,T\,\rangle_{\text{av approx}}=&\langle N_0\,|\,\mathcal{H}\,|\,T_0\rangle\\&+\tfrac{1}{2}\{(E_T-E_{T0}{}^0)+(E_N{}^U-E_{N0}{}^U)\}\,\langle N_0\,|\,T_0\rangle.\end{aligned}\qquad(6.49)$$

Numerical evaluation of the off-diagonal elements $\langle N\,|\,\mathcal{H}\,|\,T\,\rangle$ is difficult in general. For instance, if we apply this method to a diatomic molecule and choose a point between the two nuclei as origin of the united atom, then three-center integrals appear in $\langle N_0\,|\,T_0\rangle$ and $\langle N_0\,|\,\mathcal{H}\,|\,T_0\rangle$, and also we have to expect the difficulty of higher permutations due to nonorthogonal orbitals between N_0 and T_0. If we choose the position of a nucleus as the origin of the united atom, the method becomes equivalent to the ordinary separated atom approach, including an extremely high contribution of ionic structures, which is obviously not suitable for the basics. On the other hand, if we evaluate, for instance, the CH_4 molecule by the separated-atom approach, it is easy to include the united-atom functions originating at the C atom. Use of the united-atom method has been successful for this molecule.

G. Ohno's Approach[23]

After it had been pointed out that the conventional method by Moffitt, represented by Eqs. (6.26) and (6.31), is a poor approximation, alternative methods were proposed in which correlation energy and deformation of charge distribution are included; still, the calculation is as easy as in Moffitt's method because of a common z value for covalent and ionic structures. Strongly opposing such an approach, however, entirely different arguments have been published.[24] There, the deficiency of the orbital approach as pointed out by Moffitt, is considered to be due to use of unsuitable orbitals. For instance, the energy difference between ${}^3\Sigma_u{}^+$ and ${}^3\Sigma_u{}^-$ states of the O_2 molecule is calculated as 20 ev at infinite internuclear distance by using a common z for O atoms and for O^- and O^+ ions; this is a very poor result when compared with the empirical value of 11.6 ev. But if we use different z values, namely, $z(O)=4.55$, $z^+(O^+)=4.90$, and $z^-(O^-)=4.20$, the calculated value improves to 14.2 ev. These results seem to favor the view that only minor changes in the orbital functions are necessary to improve calculated values. Instead, the difficulties inherent in Moffitt's method are ascribed to the use of empirical values for the atomic energy E.

Itoh and Ohno assumed that atomic functions which give optimum energy values of free atoms and ions are the best as basics of molecular wave functions. However, according to these authors, use of any kind of empirical value should be avoided, because this may introduce uncertainty and make comparison of the results with purely theoretical values difficult. Although the Hartree-Fock functions are the best available, they assumed that Slater orbitals are good enough if we use optimum values of z for each O, O^+, and O^-, as mentioned previously. Then they evaluated the energy difference between the ${}^3\Sigma_u{}^+$ and the ${}^3\Sigma_u{}^-$ states of the O_2 molecule at the equilibrium distance and obtained reasonable agreement with the observed value.

In the calculation, however, they neglected the effect of core electrons regarding O_2 as a six-electron system. Also, they used several approximations in calculating integrals with different z values. The accuracy of the approximations is uncertain, and it is doubtful if one can ever arrive at a definite conclusion.

In order to avoid the difficulty of evaluating integrals with different z values, Ohno[23] assumed that although the use of different z values may introduce a fair amount of difference in atomic energy, this would not be so for the interatomic interaction. Therefore one can evaluate the energy matrix $\mathbf{H}^0=\mathbf{H}^0(z\neq z^+\neq z^-)$, built up from molecular wave functions with different z values, by calculating the energy matrix $\mathbf{H}^0(z)=\mathbf{H}^0(z=z^+=z^-)$, built up from ordinary functions with common z, if one calculates the energy of atoms correctly by using different z values. He then proposed to use the formula

$$[\mathbf{H}^0]_{\text{approx}}=\mathbf{H}^0(z)+\tfrac{1}{2}\{\mathbf{S}^0(z)(\mathbf{E}^0-\mathbf{E}^0(z))+(\mathbf{E}^0-\mathbf{E}^0(z))\mathbf{S}^0(z)\}, \quad (6.50)$$

where $\mathbf{H}^0(z)$, $\mathbf{S}^0(z)$, and $\mathbf{E}^0(z)$ are evaluated by using orbital functions with common z, but $\mathbf{E}^0$ is calculated using different z values. As he did not show any proof for the postulated Eq. (6.50), and it is not obvious that the energy matrix derived from it is a good approximation to $\mathbf{H}^0$, the results obtained can not be considered purely theoretical ones.

With our basics as a starting point, we investigate the validity of Eq. (6.50). The wave functions Φ_{T0} and Φ_{R0} used here with $\rho=1$ are made up from Hartree-Fock atomic functions, which satisfy Eq. (6.3). Then the energy matrix $\mathbf{H}^0$ is written exactly as

$$\begin{aligned}\mathrm{H}_{RT}{}^0=\langle R_0\,|\,\mathcal{H}\,|\,T_0\rangle&=\tfrac{1}{2}(E_T{}^0+E_R{}^0)\langle R_0\,|\,T_0\rangle\\&+\tfrac{1}{2}\{\langle R_0\,|\,\mathcal{F}_0T_0\rangle+\langle T_0\,|\,\mathcal{F}_0R_0\rangle\}\\&+\tfrac{1}{2}\{\langle R_0\,|\,\mathcal{V}T_0\rangle+\langle T_0\,|\,\mathcal{V}R_0\rangle\}. \quad (6.51)\end{aligned}$$

While the approximate functions $\Phi_{T0}(\rho)$ and $\Phi_{R0}(\rho)$, which are built up from orbitals with a common z, are used for $\mathbf{H}^0(z)$, $\mathbf{S}^0(z)$, and $\mathbf{E}^0(z)$, and also satisfy Eq. (6.3), it is found that

$$\begin{aligned}H_{RT}{}^0(\rho)=\langle R_0(\rho)\,|\,\mathcal{H}\,|\,T_0(\rho)\rangle&=\tfrac{1}{2}(E_T{}^0+E_R{}^0)\langle R_0(\rho)\,|\,T_0(\rho)\rangle\\&+\tfrac{1}{2}\{\langle R_0(\rho)\,|\,\mathcal{G}T_0(\rho)\rangle+\langle T_0(\rho)\,|\,\mathcal{G}R_0(\rho)\rangle\}\\&+\tfrac{1}{2}\{\langle R_0(\rho)\,|\,\mathcal{F}_0T_0(\rho)\rangle+\langle T_0(\rho)\,|\,\mathcal{F}_0R_0(\rho)\rangle\}\\&+\tfrac{1}{2}\{\langle R_0(\rho)\,|\,\mathcal{V}T_0(\rho)\rangle+\langle T_0(\rho)\,|\,\mathcal{V}R_0(\rho)\rangle\}.\end{aligned}$$

Also,

$$(\mathbf{E}^0(z))_T=E_{T0}(\rho)=E_0{}^{A(Q)}(\rho)+E_0{}^{B(P-Q)}(\rho)$$

$$\begin{aligned}E_0{}^{A(Q)}(\rho)&=\langle Q_0(\rho)\,|\,\mathcal{H}^A\,|\,Q_0(\rho)\rangle\\&=E_0{}^{A(Q)}+\langle Q_0(\rho)\,|\,\mathcal{G}^AQ_0(\rho)\rangle+\langle Q_0(\rho)\,|\,\mathcal{F}_0{}^AQ_0(\rho)\rangle.\end{aligned}$$

It is then easily found that

$$\begin{aligned}[E^0-E^0(z)]_T&=E_{T0}-E_{T0}(z)\\&=\lim_{R\to\infty}\{-\langle T_0(\rho)\,|\,\mathcal{G}T_0(\rho)\rangle-\langle T_0(\rho)\,|\,\mathcal{F}_0T_0(\rho)\rangle\}.\end{aligned}$$

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[23] K. Ohno, J. Phys. Soc. Japan **12,** 938 (1957).

[24] K. Ohno and T. Itoh, J. Chem. Phys. **23,** 1468 (1955); **25,** 1098 (1956).

The right-hand side of Eq. (6.50) is therefore written as

$$H_{RT}{}^0(\rho)+\tfrac{1}{2}\{(E_{T0}-E_{T0}(\rho))+(E_{R0}-E_{R0}(\rho))\}S_{RT}{}^0(\rho)$$
$$=\tfrac{1}{2}(E_T{}^0+E_R{}^0)S_{RT}{}^0(\rho)+\tfrac{1}{2}\{V_{RT}(\rho)+V_{TR}(\rho)\}$$
$$+\tfrac{1}{2}(\Delta G_{RT}+\Delta G_{TR})+\tfrac{1}{2}(\Delta F_{RT}+\Delta F_{TR}), \quad (6.52)$$

where

$$V_{RT}(\rho)=\langle R_0(\rho)\mid \mathcal{V}T_0(\rho)\rangle$$
$$\Delta G_{RT}=\langle R_0(\rho)\mid \mathcal{G}T_0(\rho)\rangle$$
$$-\langle R_0(\rho)\mid T_0(\rho)\rangle\{\lim_{R\to\infty}\langle T_0(\rho)\mid \mathcal{G}T_0(\rho)\rangle\},$$

and

$$\Delta F_{RT}=\langle R_0(\rho)\mid \mathfrak{F}_0T_0(\rho)\rangle$$
$$-\langle R_0(\rho)\mid T_0(\rho)\rangle\{\lim_{R\to\infty}\langle T_0(\rho)\mid \mathfrak{F}_0T_0(\rho)\rangle\}.$$

Now we compare Eq. (6.52) with Eq. (6.51). ΔG_{RT} and ΔF_{RT} in Eq. (6.52) are small. Although ΔG_{RT} and ΔF_{RT} are not zero, unless T_0 is an eigenfunction of the operators $\mathcal{G}$ and $\mathfrak{F}$, we assume that $\Delta G_{RT}=\Delta F_{RT}=0$. This is equivalent to Mulliken's approximation. In Eq. (6.51), $\langle R_0\mid \mathfrak{F}_0T_0\rangle$ is negligible. This approximation is an essential point of Moffitt's formula (6.17). If we assume that the molecular wave functions Φ_{T0} and $\Phi_{T0}(\rho)$ are normalized to one, then from Eqs. (6.51) and (6.52), we find that

$$\delta H=H_{RT}{}^0-H_{RT}{}^0(\rho)-\tfrac{1}{2}\{(E_{T0}-E_{T0}(\rho))$$
$$+(E_{R0}-E_{R0}(\rho))\}S_{RT}{}^0(\rho)$$
$$=\tfrac{1}{2}(E_T{}^0+E_R{}^0)\{S_{RT}{}^0-S_{RT}{}^0(\rho)\}+\tfrac{1}{2}(\Delta V_{RT}+\Delta V_{TR}),$$

where $\Delta V_{RT}=\langle R_0\mid \mathcal{V}T_0\rangle-\langle R_0(\rho)\mid \mathcal{V}T_0(\rho)\rangle$ and δH is the error expected in Eq. (6.50). For diagonal elements the error δH depends only on ΔV_{RT} and ΔV_{TR} because $S_{TT}=S_{TT}(\rho)=1$, but for off-diagonal elements both terms in δF become appreciable. Looking at tables of molecular integrals, we find that values of overlap S and interatomic interaction V change fairly rapidly with changes in z value. It is, therefore, impossible to see why δF could be negligibly small.

As pointed out in the calculation of energy levels of a C atom, it is certain that the correlation energy between electrons is appreciable and, without considering it, it is impossible to calculate the energy levels correctly. As in this method the correlation energy is omitted, we cannot expect any quantitative results, and even the order of energy levels is not given correctly. Without any example or mathematical justification, Itoh and Ohno assume that atomic wave functions in free states are the best for basics of molecular wave functions. This assumption is entirely contradictory to the results for the H_2 molecule. If we consider the interatomic interaction as perturbation and expand the energy value expression into a series of terms, and take notice of the fact that the interatomic interaction depends on the choice of atomic functions, we can see that atomic functions in the free state can not be the best ones as basics for a molecular problem. Besides, Eq. (6.50) introduces the error δH, which is not considered small; it is, therefore, doubtful if any physical significance can be attached to the method.

7. ORBITAL APPROACH

Finally, we consider the usual orbital approach on the basis of our wave function and investigate the physical meaning and mathematical reliability we can expect from results of the orbital approach calculation, and compare them to those of our approach.

In the latter, a molecular wave function Φ is obtained as a linear combination of basics Φ_T:

$$\Phi=\sum_T\Phi_T\gamma_T, \quad (7.1)$$

where the basics Φ_T are in turn built up from other basics $\Phi_K{}^0$:

$$\Phi_T=\sum_K\Phi_K{}^0c_{TK}. \quad (7.2)$$

If we take n independent basics $\Phi_K{}^0$, then we obtain at most n independent basics Φ_T, and we can always expect exactly the same result Φ, regardless of the transformation in Eq. (7.2), as long as $|c|\neq0$. We cannot, therefore, uniquely determine both sets of c_{TK} and γ_T at the same time, but we can only obtain a set of γ_T for a given set of c_{TK}. If we use only m $(m<n)$ independent functions Φ_T in Eq. (7.1), however, the result depends on the choice of c_{TK} in Eq. (7.2). If we could take a infinite number of basics $\Phi_K{}^0$ which constitute a complete set of functions, then in principle we can obtain an exact solution Φ by determining the expansion coefficients γ_T. As long as $|c|\neq0$, the transformation Eq. (7.2) can be chosen arbitrarily. Therefore, we cannot determine optimum values of c_{TK} as well as γ_T. On the other hand, if we use only a limited number m of the basics Φ_T in Eq. (7.1), then we can choose optimum values of c_{TK}, with the exception of m of these coefficients.

In Sec. 3 we proposed to build up a complete set of functions $\Phi_K{}^0$, the first term of which should be the Hartree-Fock function (case II). We have assumed that the atomic eigenfunction has been obtained so that all coefficients c_{TK} are given. In principle then we can solve the molecular problem exactly by determining γ_T in Eq. (7.1). Also, we can obtain exactly the same result Φ_T by setting $c_{TK}=\delta_{TK}$. This method corresponds to the ideal case of the traditional orbital approach. As we have already complete freedom in Φ in either case, introduction of other parameters such as the deformation correction ρ, given by Eq. (3.5), does not have any significance; instead, the difficulty of overcompleteness may come up. Special techniques, such as use of atomic eigenfunctions, do not give any particular convenience for a molecular problem, and the transformation in Eq. (7.2) has no physical or mathematical meaning, except doubling the labor of the calculation.

In practice, however, we are not able to solve a secular equation with infinite dimensions. Besides, it is not quite certain that we can set up a complete set of functions Φ_K^0 from discrete functions only. Solutions of the Schrödinger equation consist of discrete and continuous functions. If we expand a solution of the Schrödinger equation of one system by using solutions of the same equation for another system, therefore, we have to include continuous functions too. It has been proved that the Hylleraas-type functions cannot constitute a complete set of functions for the He atom. Kinoshita[11] has introduced an alternative series of functions which can be complete and still discrete. For other cases, however, discrete and complete series of functions have not yet been found except for a closed space. This means that even if we admit use of a secular equation with infinite dimensions, it is still impossible to describe our problem in the form of a secular equation because of the continuous functions.

Even if we consider discrete functions only, there is a limit to the number of functions we can take, because the error of numerical calculations accumulates. For instance, by using n functions, we obtain an energy value of E_n within an error of δE_n. If we include one more function, then the energy E_{n+1} drops. But the energy depression $E_{n+1}-E_n$ becomes smaller as the number of functions increases. Finally the energy depression becomes smaller than the error δE_n. At this point the addition of the $(n+1)$-th function becomes meaningless from the mathematical point of view. As there is no analytical way of solving a secular equation of more than three dimensions, there exists a limit to the number n of basics.

By the variational method, therefore, we are able to use only a limited number of basics Φ_T, and the results obtained depend on the choice of these basics. If we use the orbital approach by setting $c_{TK}=\delta_{TK}$, it is very difficult to take correlation energy into account, and the results will be poor as compared with the case where atomic eigenfunctions are used as basics. For instance, we may assume that 10 terms are needed to get a reasonable approximation of the He atom by the orbital approach. If we calculate a HeH molecule by the orbital approach, we have to take 10 times as many functions as we need when atomic eigenfunctions of He are used as basics. When we are interested in He_2, we would need 10×10 as many functions. This number may exceed the limiting number, and therefore we have to cut it down by omitting some functions which are mainly connected with the correlation between core electrons. Then we cannot expect results sufficiently accurate to compare with observed values because of missing this correlation energy, which is usually not small. If we calculate the lower electronic states of an O_2 molecule by orbital approach, we may expect results that are 30–40 ev higher than the observed total energies. The theoretical values of dissociation and excitation energies are defined as differences between calculated values of total energies of two O atoms and a O_2 molecule or between two O_2 molecules in different states. The error we should expect mathematically is consequently at least 40 ev. This error is much greater than the observed values of the dissociation energy ($D_e=5.08$ ev) or the lower excitation energies, which are of the order of magnitude of 1 to 10 ev. As there is no mathematical proof, that correlation energies in atoms are invariant, this way of calculating the dissociation and excitation energies is definitely unjustifiable from a theoretical point of view. In practice, the results are poor. Although D_e for the O_2 molecule is calculated as 3.6 ev, the energy difference between ${}^3\Sigma_u{}^+$ and ${}^3\Sigma_u{}^-$ is predicted as 5 ev, which is rather too large as compared with the observed value of 2 ev.[25]

TABLE III. Molecular constants of O_2 molecule by Kotani et al.

	D_e ev	Q^a a.u.	$\langle P_2/r^3\rangle$ a.u.	$\langle\Phi^2(O)\rangle$ a.u.	χ_{diam} cm³/mole
Single MO	−1.378	0.152	−0.8504	0	−31.28
SCF MO	1.027	0.132	−0.8453	0	−31.27
5 terms	3.409	−1.431	−0.8435	0	−31.85
15 terms	3.629	−1.533	−0.8589	0.1948	−31.89
Obs	5.08	$\lvert Q\rvert<0.82$	−1.32	0.187	

[a] $Q=\langle\Phi\,|\,(3\cos^2\theta-1)r^2\,|\,\Phi\rangle$.

It is certain that the calculated total energy is always above the real energy, which should be obtained from the spin-free Hamiltonian we used. The calculated energy of the ground state of the O_2 molecule by using one term has an error of about 40 ev. By using 15 terms, we gain an energy of 5 ev, but still an error of 35 ev remains. When this main part of the error is neglected, the question arises as to what physical meaning exists in this attempt of adding 14 terms plus 15^2 times the amount of labor? If we evaluate physical quantities of the O_2 molecule by using the present function, we obtain poor results as shown in Table III. The values calculated here never approach to the observed values monotonically, but some poor function can sometimes give better values than a better function.

Therefore, the calculation by the orbital approach is justified only if we assume that the correlation energy in atoms remains invariant. Then it is reasonable to evaluate the dissociation energy by taking the difference between energies calculated for two O atoms and an O_2 molecule. We can assume that the wave function with one term is unsatisfactory, because D_e obtained in this way is almost zero, whereas the function with 15 terms is better because it gives the better dissociation energy of 3.6 ev. It is not certain, however, whether the

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[25] M. Kotani et al., J. Phys. Soc. Japan **12**, 707 (1957).

calculated value of the dissociation energy is always smaller than the observed value or not. If we increase the number of functions which take correlation between valence electrons but not correlation between core electrons into account, the calculated value of the dissociation energy may converge to some value, but it can be either smaller or greater than the observed value, depending on the molecule concerned.

Empirically we can test the validity of invariance of correlation energies in atoms by comparing calculated energy values of atoms with observed ones. The results[18] show that correlation energies vary, depending on the symmetry of the electrons involved. If we neglect correlation energies in atoms by assuming that every state in atoms has a constant amount of correlation energy regardless of the state being neutral or ionic, then the differences in correlation energies come up as error in the calculation. Very often such errors are serious enough to prevent us from obtaining reasonable results. This is the main point in Moffitt's arguments, and the main reason why theoretical results are poor in practice, as seen in the calculations of the C atom and O_2 molecule.

In connection with this argument, Huzinaga[26] calculated the energy difference between the $^3\Sigma_u{}^+$ and $^1\Sigma_u{}^+$ states of the H_2 molecule. If the wave functions are built up from orbitals, the difference is calculated as 6.8 ev, which is poor as compared with the observed value of 3.8 ev. If the James-type functions are used instead, the energy of the $^1\Sigma_u{}^+$ state drops considerably, and accordingly the energy difference is evaluated as 4.6 ev, which is reasonable. This does not mean, however, that the nonempirical approach is still the most successful way for quantitative discussion of the electronic structure of molecules, and that special devices for taking correlation energy into account as developed here are not necessary. In the H_2 molecule, there are no core electrons which can introduce serious trouble in the calculation, but the other molecules do have core electrons, which we should take care of.

Huzinaga also calculated the ethylene molecule nonempirically and obtained reasonable results. But he neglected the core electrons by regarding the molecule as consisting of two π electrons traveling around effective nuclei with nuclear charges $Z=2$ or $Z=3$. As many authors have pointed out,[27] the effect of core electrons is comparable with the interaction between valence electrons, and results obtained by neglecting the effect are not reliable. In fact, the results of Huzinaga do not represent the energy levels of the ethylene molecule, but correspond more or less to the energy levels of $He_2{}^{++}$ or $Be_2{}^{4+}$ in extremely high excited states, because the results are approximate solutions of the Schrödinger equation of a two-electron system with nuclear charges $Z=2$ or 3. As the states in which both electrons are promoted to $2p$ orbitals belong to continuous levels, the results cannot have any physical meaning unless we give additional conditions which can specify the difference between C_2H_6 and $He_2{}^{++}$ or $Be_2{}^{4+}$. The effect of core electrons will be considered in another paper.

In our method, the wave function used is the one given by Eqs. (7.1) and (7.2). Although it is impossible to solve Eq. (7.2) by the variational method, all coefficients c_{TK} would be determined correctly by

$$c_{TK}=\int \Phi_K{}^{0*}\Phi_T d\tau,$$

if exact solutions Φ_T could exist. Then the calculated energy is certainly above the observed total energy, and moreover its value is comparable to the observed value so that it is quite possible to discuss the accuracy of the wave function obtained purely theoretically. Unfortunately, there is no exact solution for atoms, and then the energy matrix can be evaluated only approximately. The method suggested in Eq. (6.1) is to calculate the main part of the matrix elements accurately, but to evaluate other parts approximately, so that we are able to calculate the total energy matrix up to a certain decimal point. Because of the approximation it may happen that the calculated value goes down below the observed value; the variational principle holds only within the limit of numerical accuracy of the approximation. If the approximation mentioned in Eq. (6.1) is not good enough, however, it is always possible to increase the accuracy by adding more terms in calculating S, V, G, and F integrals.

In our method, physical properties other than energy values are also calculated, because the molecular wave function is defined mathematically. In practice, we have to expand them by using Eq. (7.2). Here we can evaluate the atomic problem more exactly and calculate the effect of the interatomic interaction approximately so that we are able to obtain more reliable values than the results obtained by the orbital approach. For instance, the field gradient q at a nucleus in the Li_2 molecule has been evaluated with satisfactory accuracy.[6] On the other hand, the orbital approach cannot even give the correct sign of the q value.

In conclusion, the difference between our approach and the orbital approach is in the different ways of cutting off the series expansion of the wave function in Eqs. (7.1) and (7.2). In the orbital approach, however, the basics are so poor that we have to depend on an empirical assumption in order to make the results physically sensible. The results are therefore not purely theoretical; in fact, the assumption used is quite doubtful. In our method the basics may be satisfactory but too complicated to use for calculating the energy matrix exactly. We have to use some approximation in numerical calculations. Because of the approximation

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[26] S. Huzinaga, Progr. Theor. Phys. (Kyoto) **20**, 15 (1958).

[27] Originally by H. M. James, J. Chem. Phys. **2**, 794 (1934).

there is a limit to the accuracy. However, use of spectroscopic data for evaluating atomic energies will help, but is not at all essential from a theoretical point of view.

In a forthcoming paper, we shall discuss how our approach can be simplified for application to more complicated systems. We shall consider the accuracy of further approximation by comparing with the corresponding simplification in the orbital approach.

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Electronic Structure and Binding Energy of Carbon Monoxide

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1. INTRODUCTION

THE most accurate method of determining dissociation energies of diatomic molecules is from the analysis of their band spectra. In favorable cases, when this analysis is unambiguous, values accurate to within 0.001 ev may be obtained [e.g., O_2 Herzberg (1950)[1]]. However, for many molecules of thermochemical interest the analysis of the spectra is ambiguous and leads to several possible values for the dissociation energy. One of the most important examples of this is provided by the carbon monoxide molecule. Here the spectroscopic data are consistent with just three values for $D_e(\mathrm{CO})$, namely, 9.28 ev [Herzberg (1950)], 9.74 ev [Hagstrum (1947)], and 11.24 ev [Gaydon (1947)].

In this situation, relatively crude estimates of the dissociation energy may be of value in distinguishing between the possible spectroscopic values. Various experimental techniques have been employed for this purpose; for example, mass-spectrometric analysis of the ions resulting from the electron bombardment of carbon monoxide [Hagstrum (1951, 1955)] and the direct thermochemical measurement of the latent heat of sublimation of graphite [Chupka and Inghram (1953, 1955)], this quantity being related to $D_0(\mathrm{CO})$ by well-established thermochemical quantities.

In this paper two theoretical calculations of the binding energy and ground state wave function of carbon monoxide are described. The first is an *ab initio* orbital calculation and the second employs the intra-atomic correlation correction (ICC), introduced by the author [Hurley (1956a, 1958a)], as a necessary modification of the method of atoms in molecules [Moffitt (1951)], The orbital calculation (Sec. 2) is carried out in such a way as to facilitate the transition to the ICC theory in later sections. The key quantity in this transition is the transformation matrix T [Eq. (2.21)].

2. ORBITAL CALCULATION

(a) Atomic Orbitals

The basic atomic orbitals are taken as orthogonalized Slater-type functions centered on the carbon and oxygen nuclei.

$$\begin{aligned}
\sigma\text{-type}\quad & \phi_1=k_O=(\zeta_1^3/\pi)^{\frac{1}{2}}\exp(-\zeta_1 r_O),\\
& \phi_2=k_C=(\zeta_2^3/\pi)^{\frac{1}{2}}\exp(-\zeta_2 r_C),\\
& \phi_3=s_O=N_1\{(\zeta_3^5/3\pi)^{\frac{1}{2}} r_O\exp(-\zeta_3 r_O)-\alpha_1 k_O\},\\
& \phi_4=s_C=N_2\{((\zeta_4^5/3\pi)^{\frac{1}{2}} r_C\exp(-\zeta_4 r_C)-\alpha_2 k_C\},\\
& \phi_5=\sigma_O=(\zeta_5^5/\pi)^{\frac{1}{2}} z_O\exp(-\zeta_5 r_O), \qquad (2.1)\\
& \phi_6=\sigma_C=(\zeta_6^5/\pi)^{\frac{1}{2}} z_C\exp(-\zeta_6 r_C),\\
x\text{-type}\quad & \phi_7=x_O=(\zeta_5^5/\pi)^{\frac{1}{2}} x_O\exp(-\zeta_5 r_O),\\
& \phi_8=x_C=(\zeta_6^5/\pi)^{\frac{1}{2}} x_C\exp(-\zeta_6 r_C),\\
y\text{-type}\quad & \phi_9=y_O=(\zeta_5^5/\pi)^{\frac{1}{2}} y_O\exp(-\zeta_5 r_O),\\
& \phi_{10}=y_C=(\zeta_6^5/\pi)^{\frac{1}{2}} y_C\exp(-\zeta_6 r_C).
\end{aligned}$$

Here (x_O,y_O,z_O), (x_C,y_C,z_C) are Cartesian coordinates centered on the oxygen and carbon nuclei; the z axes are directed inwards along the internuclear axis and the $x,(y)$ axes on the two centers are parallel:

$$r_O=(x_O^2+y_O^2+z_O^2)^{\frac{1}{2}},\quad r_C=(x_C^2+y_C^2+z_C^2)^{\frac{1}{2}}.$$

The orbital exponents ζ have values which minimize the energy of the ground state dissociation products $\mathrm{O}(s^2p^4, {}^3P)$, $\mathrm{C}(s^2p^2, {}^3P)$ [Roothaan (1955)].

$$\begin{aligned}
&\mathrm{O}:\ \zeta_1=7.66,\quad \zeta_3=2.25,\quad \zeta_5=2.23,\\
&\mathrm{C}:\ \zeta_2=5.67,\quad \zeta_4=1.61,\quad \zeta_6=1.57. \qquad (2.2)
\end{aligned}$$

All the basic atomic integrals involving the orbitals (2.1) were evaluated for the equilibrium nuclear separation $R=2.1319$ atomic units (a.u.) [Herzberg (1950)], and are listed in Appendix II.

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[1] References are given in alphabetical order in the Bibliography.