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An approximate relation between Wigner–Seitz-type one-electron Hamiltonians and complete Hamiltonians for molecules and solids

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Summary. The relation between the sum of Wigner–Seitz-type one-electron Hamiltonians of all electrons in a system (any molecule or solid) and the complete Hamiltonian for the system is deduced. According to this relation, the total energy for an electronic configuration may be formulated approximately as a quadratic function of the atomic charges defined for the configuration added to the sum of the energies of occupied orbitals. This formula is necessary for evaluating the system's total energy, using the orbital energies calculated from the Wigner–Seitz-type potential (called the linkage of embedded atomic fields (LEAF)), and is also useful for analyzing and understanding electronic structures, reactivities, and other properties of molecules and solids.

Key words: Total energy – Extended Hückel

1. Introduction

The independent particle model (IPM) is certainly a bad approximation for many systems (molecules or solids), but it is nevertheless essentially helpful for analyzing and understanding electronic structures, reactivities, and other properties. In the IPM, total energies of a system are equal to the sums of the orbital energies of all electrons in the system. Hückel theories are applications of this equation to molecules and have greatly assisted our understanding of molecules (e.g., [1]). However, the applicability of total energy equation is limited [2]. Thus, people usually use the Hartree–Fock molecular orbital method and its derivatives, which are applicable to the ground states of all molecules. Unfortunately, these methods abandon the merit of the IPM: the orbital varies as a function of electronic states and the relation between orbital energies and total energies is generally complicated. This is very inconvenient for analyzing and understanding electronic structures.

It would be useful to have a molecular orbital theory in which the orbitals are calculated from a given one-electron potential, as in noniterative Hückel theories, and the total energy in every electronic state can be calculated by adding a simple correction term to the sum of the orbital energies. The Wigner–Seitz-type potential, called the linkage of embedded atomic fields

(LEAF), is similar to the one-electron potential in the extended Hückel (EH) theories and the Wigner–Seitz method [3, 4]. This paper deductively reveals the approximate relation between the complete Hamiltonian and LEAF one-electron Hamiltonians for any molecule or solid, or between the total energies and LEAF orbital energies of the system. The present approximate form of the total energy for an electronic configuration is the sum of the occupied LEAF orbital energies added to a simple function of atomic charges defined for the configuration. It therefore enables an intelligible analysis of various electronic states in terms of the orbitals and atomic charges.

2. Derivation

2.1. Definition of Hamiltonians

The complete Hamiltonian (or the total-energy operator) for a system, which consists of N_n fixed nuclei and N_e electrons, is defined as

$$\hat{H} \equiv \hat{T} + V, \tag{1}$$

where $\hat{T}$ is the kinetic energy of electrons in the system represented as

$$\hat{T} \equiv \sum_{\mu=1}^{N_e} -\hbar^2/2m(\partial^2/\partial x_\mu^2 + \partial^2/\partial y_\mu^2 + \partial^2/\partial z_\mu^2), \tag{2}$$

and V is the potential term represented as

$$V \equiv \sum_{\alpha=1}^{N_n} \sum_{\mu=1}^{N_e} (-Z_\alpha e^2)/|\boldsymbol{r}_\mu - \boldsymbol{R}_\alpha| + (1/2) \sum_{\substack{\mu=1\\(\mu\neq\nu)}}^{N_e} \sum_{\nu=1}^{N_e} e^2/|\boldsymbol{r}_\mu - \boldsymbol{r}_\nu|$$
$$+ (1/2) \sum_{\substack{\alpha=1\\(\alpha\neq\beta)}}^{N_n} \sum_{\beta=1}^{N_n} Z_\alpha Z_\beta e^2/|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|, \tag{3}$$

where μ is the label for the μth electron in the system, α is the label for the αth nucleus in the system, $\boldsymbol{r}_\mu = (x_\mu, y_\mu, z_\mu)$ the position vector of the μth electron, $\boldsymbol{R}_\alpha$ the position vector of the αth nucleus, and $Z_\alpha e$ the charge of the αth nucleus.

The LEAF (or Wigner–Seitz-type potential) $v(\boldsymbol{r})$ is defined as

$$v(\boldsymbol{r}) = v_\alpha(\boldsymbol{r}) \quad (\text{when } \boldsymbol{r} \in C_\alpha), \tag{4}$$

where C_α is a three-dimensional (3D) region, which could include most of the electron cloud of the imaginary free atom that has the same type nucleus at the same position as the αth nucleus and also has Z_α electrons, whose configuration is most stable; where $v_\alpha(\boldsymbol{r})$ is the potential that reproduces the Hartree–Fock orbitals in the free atom. None of the 3D-region pairs (C_α and C_β) overlaps, and the sum of the 3D regions is the region in which electron movement is contained (Fig. 1). Naturally, the one-electron Hamiltonian based on the LEAF potential is defined as

$$\hat{h}(\mu) \equiv (-\hbar^2/2m)(\partial^2/\partial x_\mu^2 + \partial^2/\partial y_\mu^2 + \partial^2/\partial z_\mu^2) + v(\boldsymbol{r}_\mu). \tag{5}$$

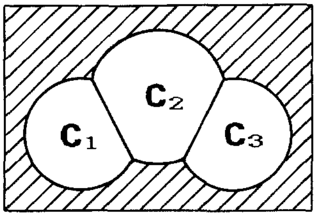

Fig. 1. Illustration of 'cells' in a system. The *shaded region* denotes the outside of the molecule, into which no electron is assumed to enter. C_1, C_2, and C_3 are the atomic cell labels in a triatomic molecule

According to this definition of the 3D region, C_α may be called an atomic region or atomic cell. The 3D regions are not completely defined here because only the number of electrons in each region is needed for the present derivation and for the actual calculations of the system's total energy.

2.2. *Rewriting of potential terms in the complete Hamiltonian*

Here, each atomic cell is divided into a core region and a valence region. The core region is defined as a 3D region that includes most of the core-electron cloud of the imaginary free atom, and the valence region is defined as the remaining region of the atomic cell (Fig. 2). For simplicity, electron movements will be discussed based on the classical picture; this is valid as long as the potential terms of the complete Hamiltonians are discussed because the potential terms are functions of electron positions only.

First, all the core electrons are assumed to be frozen in each core region. Second, a new set of electron labels in the system is introduced. Classically, at a given time, the number of electrons in each 3D region can be counted: $Z_{\alpha c}$ electrons in the core region of the atomic cell C_α and $(Z_{\alpha v} + K_\alpha)$ electrons in the valence region of C_α, where $Z_{\alpha c}$ and $Z_{\alpha v}$ stand for the number of core and valence electrons in the ground-state neutral free atom, respectively, and K_α is a variable integer which denotes the excess number of electrons in C_α. We give the ith electron in the core region of C_α the label

$$\langle \alpha i \rangle \quad (i = 1, 2, \ldots, Z_{\alpha c}), \tag{6}$$

and the ith electron in the valence region of C_α the label

$$[\alpha i] \quad (i = 1, 2, \ldots, Z_{\alpha v} + K_\alpha). \tag{7}$$

Utilizing labels (6) and (7), one can rewrite the potential terms of the complete Hamiltonian (Eq. (3)) as

$$\begin{aligned}
V = {} & \sum_{\alpha=1}^{N_\mathrm{n}} \sum_{\beta=1}^{N_\mathrm{n}} \left\{ \sum_{i=1}^{Z_{\beta c}} (-Z_\alpha e^2)/|\boldsymbol{r}_{\langle \beta i \rangle} - \boldsymbol{R}_\alpha| + \sum_{i=1}^{Z_{\beta v}+K_\beta} (-Z_\alpha e^2)/|\boldsymbol{r}_{[\beta i]} - \boldsymbol{R}_\alpha| \right\} \\
& + (1/2) \sum_{\substack{\alpha=1 \\ (\alpha \neq \beta)}}^{N_\mathrm{n}} \sum_{\beta=1}^{N_\mathrm{n}} \left\{ \sum_{i=1}^{Z_{\alpha c}} \sum_{j=1}^{Z_{\beta c}} e^2/|\boldsymbol{r}_{\langle \alpha i \rangle} - \boldsymbol{r}_{\langle \beta j \rangle}| + \sum_{i=1}^{Z_{\alpha c}} \sum_{j=1}^{Z_{\beta v}+K_\beta} e^2/|\boldsymbol{r}_{\langle \alpha i \rangle} - \boldsymbol{r}_{[\beta j]}| \right. \\
& \left. + \sum_{i=1}^{Z_{\alpha v}+K_\alpha} \sum_{j=1}^{Z_{\beta c}} e^2/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{r}_{\langle \beta j \rangle}| + \sum_{i=1}^{Z_{\alpha v}+K_\alpha} \sum_{j=1}^{Z_{\beta v}+K_\beta} e^2/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{r}_{[\beta j]}| \right\} \\
& + \sum_{\alpha=1}^{N_\mathrm{n}} \left\{ (1/2) \sum_{\substack{i=1 \\ (i \neq j)}}^{Z_{\alpha c}} \sum_{j=1}^{Z_{\alpha c}} e^2/|\boldsymbol{r}_{\langle \alpha i \rangle} - \boldsymbol{r}_{\langle \alpha j \rangle}| + \sum_{i=1}^{Z_{\alpha c}} \sum_{j=1}^{Z_{\alpha v}+K_\alpha} e^2/|\boldsymbol{r}_{\langle \alpha i \rangle} - \boldsymbol{r}_{[\alpha j]}| \right. \\
& \left. + (1/2) \sum_{\substack{i=1 \\ (i \neq j)}}^{Z_{\alpha v}+K_\alpha} \sum_{j=1}^{Z_{\alpha v}+K_\alpha} e^2/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{r}_{[\alpha j]}| \right\} + (1/2) \sum_{\substack{\alpha=1 \\ (\alpha \neq \beta)}}^{N_\mathrm{n}} \sum_{\beta=1}^{N_\mathrm{n}} Z_\alpha Z_\beta e^2/|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|.
\end{aligned} \tag{8}$$

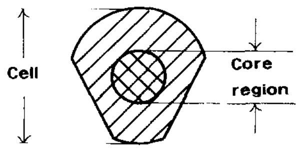

Fig. 2. Illustration of a core region and a valence region. ▩, Core region; ▨ valence region

To simplify Eq. (8), we first take the following approximations for the distances between the particles located in different cells:

$$|\boldsymbol{r}_{\langle\beta i\rangle} - \boldsymbol{R}_\alpha| \sim |\boldsymbol{R}_\beta - \boldsymbol{R}_\alpha| \qquad (\alpha \neq \beta), \tag{9}$$

$$|\boldsymbol{r}_{[\beta i]} - \boldsymbol{R}_\alpha| \sim |\boldsymbol{R}_\beta - \boldsymbol{R}_\alpha| \qquad (\alpha \neq \beta), \tag{10}$$

$$|\boldsymbol{r}_{\langle\alpha i\rangle} - \boldsymbol{r}_{\langle\beta j\rangle}| \sim |\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta| \qquad (\alpha \neq \beta), \tag{11}$$

$$|\boldsymbol{r}_{\langle\alpha i\rangle} - \boldsymbol{r}_{[\beta j]}| \sim |\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta| \qquad (\alpha \neq \beta), \tag{12}$$

$$|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{r}_{[\beta j]}| \sim |\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta| \qquad (\alpha \neq \beta). \tag{13}$$

When the distance between the nuclei in question is very short, the approximations of (9)–(13) are poor; these approximations will be discussed and modified later. Second, we approximate the distances between the core electrons and the valence electrons in one cell by

$$|\boldsymbol{r}_{[\alpha j]} - \boldsymbol{r}_{\langle\alpha i\rangle}| \sim |\boldsymbol{r}_{[\alpha j]} - \boldsymbol{R}_\alpha|. \tag{14}$$

Third, we approximate the interaction between core electrons in one core region by

$$e^2/|\boldsymbol{r}_{\langle\alpha i\rangle} - \boldsymbol{r}_{\langle\alpha j\rangle}| \sim \gamma_{\alpha c} \tag{15}$$

and that between valence electrons in one valence region by

$$e^2/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{r}_{[\alpha j]}| \sim \gamma_{\alpha v}, \tag{16}$$

where $\gamma_{\alpha c}$ and $\gamma_{\alpha v}$ are constant values. Introducing approximations (9)–(16) into the description of V in Eq. (8), one then obtains

$$\begin{aligned} V \sim & \sum_{\alpha=1}^{N_n} \left\{ \sum_{i=1}^{Z_{\alpha c}} (-Z_\alpha e^2)/|\boldsymbol{r}_{\langle\alpha i\rangle} - \boldsymbol{R}_\alpha| + \sum_{i=1}^{Z_{\alpha v}+K_\alpha} (-Z_{\alpha v} e^2)/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{R}_\alpha| \right\} \\ & + (1/2) \sum_{\substack{\alpha=1 \\ (\alpha\neq\beta)}}^{N_n} \sum_{\beta=1}^{N_n} K_\alpha K_\beta e^2/|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta| \\ & + \sum_{\alpha=1}^{N_n} (1/2)(Z_{\alpha v} + K_\alpha)(Z_{\alpha v} + K_\alpha - 1)\gamma_{\alpha v} + \sum_{\alpha=1}^{N_n} (1/2) Z_{\alpha c}(Z_{\alpha c} - 1)\gamma_{\alpha c}. \end{aligned} \tag{17}$$

Here, we discuss the replacement of the intercellular interaction in Eq. (17), $(K_\alpha K_\beta e^2/|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|)$, with another appropriate form because the discrepancy between the position of a nucleus and the effective center of the cell (electrons and the nucleus) cannot be neglected when the distance between the nuclei in question is very short. To account for the above discrepancy, we introduce simple model for the intercellular interaction $V_{\alpha\beta}$:

$$V_{\alpha\beta} = K_\alpha K_\beta e^2/f_{\alpha\beta}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|), \tag{18}$$

where the function $f_{\alpha\beta}$ is defined by

$$f_{\alpha\beta}(X) \equiv \begin{cases} R_{\alpha\beta c} & (X \leqslant R_{\alpha\beta c}) \\ X & (X \geqslant R_{\alpha\beta c}), \end{cases} \tag{19}$$

and $R_{\alpha\beta c}$ denotes the minimum value of the $|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|$s at which the approximations of (9)–(13) are valid.

2.3. Introduction of potentials for atomic orbitals

The one-electron potential of a neutral free atom can be written as

$$v_\alpha(r) = (-Z_\alpha e^2)/|\boldsymbol{r} - \boldsymbol{R}_\alpha| + G_\alpha(\boldsymbol{r}), \tag{20}$$

where the local function $G_\alpha(\boldsymbol{r})$ is the repulsive potential originating from other electrons in the atom. Here, one may introduce the following approximations:

$$G_\alpha(\boldsymbol{r}_{\langle\alpha i\rangle}) \sim (Z_{\alpha c} - 1)\gamma_{\alpha c} + Z_{\alpha v}\gamma_{\alpha c v} \tag{21}$$

and

$$G_\alpha(\boldsymbol{r}_{[\alpha i]}) \sim (Z_{\alpha v} - 1)\gamma_{\alpha v} + Z_{\alpha c}e^2/|\boldsymbol{r}_{[\alpha i]} - \boldsymbol{R}_\alpha|, \tag{22}$$

where the value of the repulsive potential between a core electron and a valence electron is replaced with a constant value ($\gamma_{\alpha c v}$) in Eq. (21).

Replacing the intercellular terms in Eq. (17) with the new one of Eq. (18), rewriting the electron-nucleus terms in Eq. (17) by using Eq. (20) with approximations of (21) and (22), and changing the electron labels by using the definition of LEAF potential (Eq. (4)), one derives the following approximate relation between v and V.

$$\begin{aligned} V \sim & \sum_{\mu=1}^{N_e} v(\boldsymbol{r}_\mu) + \sum_{\alpha=1}^{N_n} (1/2)K_\alpha(K_\alpha + 1)\gamma_{\alpha v} \\ & + (1/2) \sum_{\alpha=1}^{N_n} \sum_{\substack{\beta=1 \\ (\alpha \neq \beta)}}^{N_n} K_\alpha K_\beta \, e^2/f_{\alpha\beta}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|) + \text{const}, \end{aligned} \tag{23}$$

where ‘const’ is invariant, and is specified by

$$\text{const} \equiv - \sum_{\alpha=1}^{N_n} (1/2)Z_{\alpha v}(Z_{\alpha v} - 1)\gamma_{\alpha v} - \sum_{\alpha=1}^{N_n} (1/2)Z_{\alpha c}(Z_{\alpha c} - 1)\gamma_{\alpha c} - \sum_{\alpha=1}^{N_n} Z_{\alpha v}Z_{\alpha c}\gamma_{\alpha c v}. \tag{24}$$

From the definition of $\hat{H}$ and $\hat{h}$ (Eqs. (1) and (5)), one obtains an approximate relation between the complete Hamiltonian and LEAF one-electron Hamiltonians for a system as

$$\begin{aligned} \hat{H} \sim & \sum_{\mu=1}^{N_e} \hat{h}(\mu) + \sum_{\alpha=1}^{N_n} (1/2)K_\alpha(K_\alpha + 1)\gamma_{\alpha v} \\ & + (1/2) \sum_{\alpha=1}^{N_n} \sum_{\substack{\beta=1 \\ (\alpha \neq \beta)}}^{N_n} K_\alpha K_\beta \, e^2/f_{\alpha\beta}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|) + \text{const}. \end{aligned} \tag{25}$$

3. Physical meaning of the relation between $\hat{H}$ and $\hat{h}$

The eigenvalue of the $\hat{H}$, i.e., the total energy of a system, can be calculated approximately by utilizing Eq. (25). First, the right-hand side of Eq. (25) is divided into the sum of an uperturbed term,

$$\hat{H}_{(0)} \equiv \sum_{\mu=1}^{N_e} \hat{h}(\mu) + \text{const}, \tag{26}$$

and a perturbation term,

$$\hat{H}' \equiv \sum_{\alpha=1}^{N_n} (1/2)K_\alpha(K_\alpha+1)\gamma_{\alpha v} + (1/2)\sum_{\substack{\alpha=1 \\ (\alpha\neq\beta)}}^{N_n}\sum_{\beta=1}^{N_n} K_\alpha K_\beta\, e^2/f_{\alpha\beta}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|). \tag{27}$$

Let the eigenfunctions of $\hat{h}$ be $\{\phi_i\}$ and let the eigenvalues of $\hat{h}$ be $\{\varepsilon_i\}$. The eigenvalues of $\hat{H}_{(0)}$ are various sums of ε_is represented as

$$E_{J(0)} = \sum_{i=1}^{\alpha} v_i\varepsilon_i + \text{const}, \tag{28}$$

where d denotes the dimension of $\{\phi_i\}$, v_i the number of the electrons which occupy the orbital of ϕ_i ($v_i = 0$, 1, or 2), and the letter J the electronic configuration ($\Phi_{J(0)}$) characterized by $\{v_1, v_2, \ldots, v_d\}$. According to first-order many-body perturbation theory, one obtains the total energy of the system from Eqs. (25)–(28) as

$$E_J \sim E_{J(0)} + E_{J(1)AA} + E_{J(1)AB}, \tag{29}$$

where $E_{J(1)AA}$ and $E_{J(1)AB}$ are defined by

$$E_{J(1)AA} \equiv \sum_{\alpha=1}^{N_n} (1/2)Q_{J\alpha}(Q_{J\alpha}-1)\gamma_{\alpha v} \tag{30}$$

and

$$E_{J(1)AB} \equiv (1/2)\sum_{\substack{\alpha=1 \\ (\alpha\neq\beta)}}^{N_n}\sum_{\beta=1}^{N_n} Q_{J\alpha}Q_{J\beta}\, e^2/f_{\alpha\beta}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|), \tag{31}$$

respectively, where $Q_{J\alpha}$ denotes the expectation value of $-K_\alpha$ for the electronic configuration $\Phi_{J(0)}$, i.e. $\langle\Phi_{J(0)}|-K_\alpha|\Phi_{J(0)}\rangle$, and the statistical variances of K_αs and the covariances of (K_α, K_β)s are neglected.

According to the definition of K_α in Sect. 2.2, the physical meaning of $Q_{J\alpha}e$ is the charge of C_α for $\Phi_{J(0)}$, or the zeroth-order atomic charge. Thus in the case where the system has neither charge nor polarity, i.e. $Q_{J\alpha} = 0$ for every α,

$$E_J \sim E_{J(0)}, \tag{32}$$

as can be determined from Eqs. (29)–(31). Therefore, generally speaking, the $E_{J(0)}$ term of E_J may be related to the covalent or metallic bonds in the system. Equation (32) may also justify the procedure for evaluating cohesive energies of alkali metals in the Wigner–Seitz method [3] and the foundation of the Hückel theory [5]. Equation (30) shows that the $E_{J(1)AA}$ term can describe the increase of electron-electron repulsion originating in the negative charges of cells.[1] Finally, Eq. (31) directly shows that $E_{J(1)AB}$ is strongly related to the ionic bond character.

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[1] $E_{J(1)AA}$ consists of the quadratic functions of atomic charges, which have been used to correct the valence orbital ionization potentials (VOIP), i.e. atomic orbital energies in iterative EH theories. In the present formulation, the functions work as one of the first-order many-body corrections for total energy, using the zeroth-order atomic charges

4. Applications

4.1. Procedure

The details of the calculations of molecular orbitals and cellular charges are described in Appendix A1. The atomic parameters, $e_{\alpha nl}$ and $\gamma_{\alpha v}$, were evaluated from atomic spectra [6] (see Appendix A2), and the Slater exponents of atomic orbitals (AOs) were taken from Hartree–Fock calculations of atoms [7]. The atomic parameters are shown in Table 1, while the $\gamma_{\alpha v}$s for N and O are not necessary in the present applications. The $R_{\alpha\beta c}$s (Eq. (19)) used here are 0.92 Å for the H–F pair, 1.66 Å for the H–Ga pair, and 1.50 Å for the H–As pair.

4.2. Equilibrium internuclear distances of homonuclear diatomic molecules

In the case of homonuclear diatomic molecules in the ground state, the total energy is simply equal to $E_{J(0)}$ (Eq. (28)) because the atomic charges ($Q_{J\alpha}$) are all zeros. Such a formula for the total energy has been employed in the EH molecular orbital (MO) calculations [1]. Thus we can compare the MO calculations based on LEAF with those based on the matrix element of a conventional EH Hamiltonian (Wolfsberg–Helmholtz formula [8], see Appendix A3).

Table 2 lists the equilibrium internuclear distances (r_e) of some homonuclear diatomic molecules in their ground state (H_2, N_2, O_2, and As_2), calculated by minimizing the total energies of Eq. (29). This table also includes the experimental r_es and the results of the conventional EH calculation. All r_es calculated by the present method (LEAF) compare well with experimental data.[2] This result proves the soundness of the derivation of the LEAF total-energy formula.

Table 1. Atomic parameters

Element	$\gamma_{\alpha v}$/eV	Valence AO	$\zeta_{\alpha nl}$[a]	$e_{\alpha nl}$/eV
H	17.00[b]	1*s*	1.0000	−13.60
N		2*s*	1.9237	−25.57
		2*p*	1.9170	−13.19
O		2*s*	2.2459	−32.37
		2*p*	2.2266	−15.84
F	19.12	2*s*	2.5639	−37.86
		2*p*	2.5500	−18.65
Ga	8.31	4*s*	1.7670	−12.20
		4*p*	1.5549	−5.93
As	10.52	4*s*	2.2307	−18.20
		4*p*	1.8932	−9.19

[a] $\zeta_{\alpha nl}$ denotes the exponent of a Slater-type atomic orbital
[b] $\gamma_{\alpha v}$ for H is the one-center electronic repulsion integral $(1s1s|1s1s)$

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[2] The reason why the nuclei of H_2 do not unite in the calculation with the LEAF method, in contrast with the EH method, is that the LEAF method incorporates the 'quantum size effect', i.e. the effect that the kinetic energy of electrons increases as the length of the 1σ orbital decreases (see Appendices A1 and A3)

Table 2. Calculated and experimental internuclear distances[a] of homonuclear diatomic molecules in the ground state

Molecule	Present work (LEAF)	EH[b]	Experimental[c]
H_2	0.83	0.00	0.74
N_2	1.13	0.87	1.10
O_2	1.16	1.52	1.21
As_2	1.92	1.69	2.10

[a] Units: Å

[b] Based on the Wolfsberg–Helmholtz formula ($K = 1.75$)

[c] Huber KP, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand Reinhold

4.3. Importance of the first-order correction for determining the equilibrium internuclear distance of a GaH *molecule*

Figure 3 shows the variations of the total energy ($E_G = E_{G(0)} + E_{G(1)AA} + E_{G(1)AB}$), of the zeroth-order term ($E_{G(0)}$), and of the first-order term ($E_{G(1)} \equiv E_{G(1)AA} + E_{G(1)AB}$) of the GaH molecule in the ground state, all as functions of the internuclear distance. The minimum of the first-order-corrected total energy ($E_G = E_{G(0)} + E_{G(1)}$) approximately corresponds to the experimental r_e of GaH (1.66 Å). However the internuclear distance for the minimum $E_{G(0)}$ is far longer than that for the minimum E_G (~0.4 Å). Thus the first-order correction is very important in determining the r_e of GaH in the ground state.

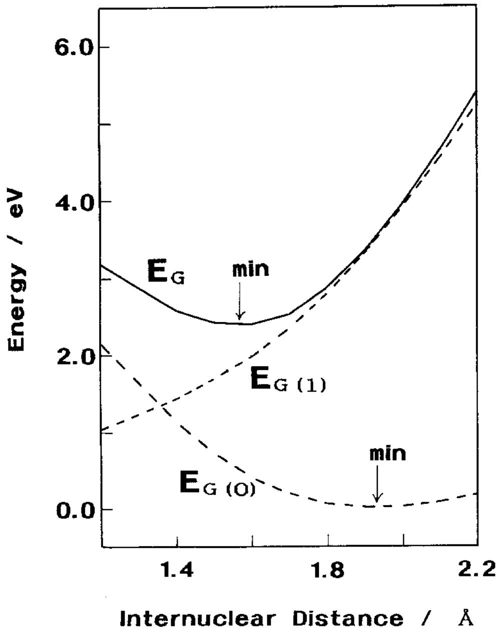

Fig. 3. Importance of the first-order correction in determining the equilibrium internuclear distance of GaH in its ground state. $E_G \equiv E_{G(0)} + E_{G(1)}$. $E_{G(1)} \equiv E_{G(1)AA} + E_{G(1)AB}$

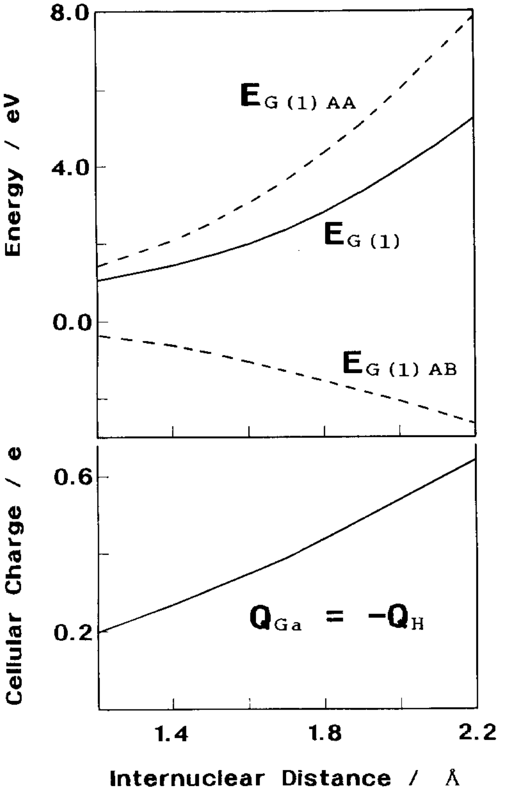

Fig. 4. Analysis of the $E_{G(1)}$ curve for GaH. $E_{G(1)} \equiv E_{G(1)AA} + E_{G(1)AB}$

In Fig. 4, $E_{G(1)}$ is divided into $E_{G(1)AA}$ and $E_{G(1)AB}$, and the variation of cellular charge ($Q_{\mathrm{Ga}} = -Q_{\mathrm{H}}$) is shown. First, Fig. 4 shows that the increasing character of the $E_{G(1)}$ comes from that of the $E_{G(1)AA}$. Second, analyzing the formula for $E_{G(1)AA}$ (Eq. (30)) and the Q curve, it is found that the electronic repulsion orginating from the negative charge of the H cell causes the attractive characters of $E_{G(1)AA}$ and $E_{G(1)}$.

4.4. Importance of the first-order correction to potential energy curves for various configurations of AsH *and* FH *molecules*

Figures 5 and 6 show the potential energy curves for the various electronic configurations of AsH and FH molecules, respectively. The minima of both the zeroth-order and the first-order-corrected total energies of configuration I (representing the ground state) of AsH and FH correspond to the experimental r_es, 1.53 Å and 0.92 Å, respectively. Also, the energy levels of configuration II of FH, measured from configuration I at r_e, (11.68 eV in the zeroth order and 10.24 eV in the first order) are consistent with the $(1\pi \rightarrow 4\sigma)$ excitation energy calculated by reliable CI methods ($\sim$10.2 eV) [9].[3]

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[3] This excellent result for the excitation energy is attributed to the character of the approximate LEAF one-electron Hamiltonians (A3), the eigenvalue problem of which can be solved exactly, and all the eigenvalues (i.e. the orbital energies) of which are negative (see Appendix A1 and [4])

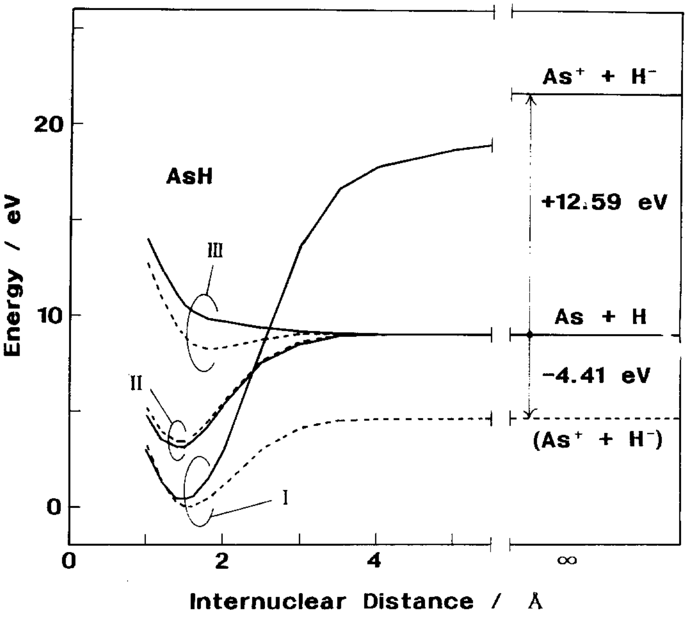

Fig. 5. Calculated potential energy curves for various configurations of AsH. *Broken line*: $E_{J(0)}$; *solid line*: $E_{J(0)} + E_{J(1)AA} + E_{J(1)AB}$. I: [core] $(7\sigma)^2(8\sigma)^2(4\pi)^2$; II: [core] $(7\sigma)^2(8\sigma)^1(4\pi)^3$; III: [core] $(7\sigma)^2(8\sigma)^1(4\pi)^2(9\sigma)^1$

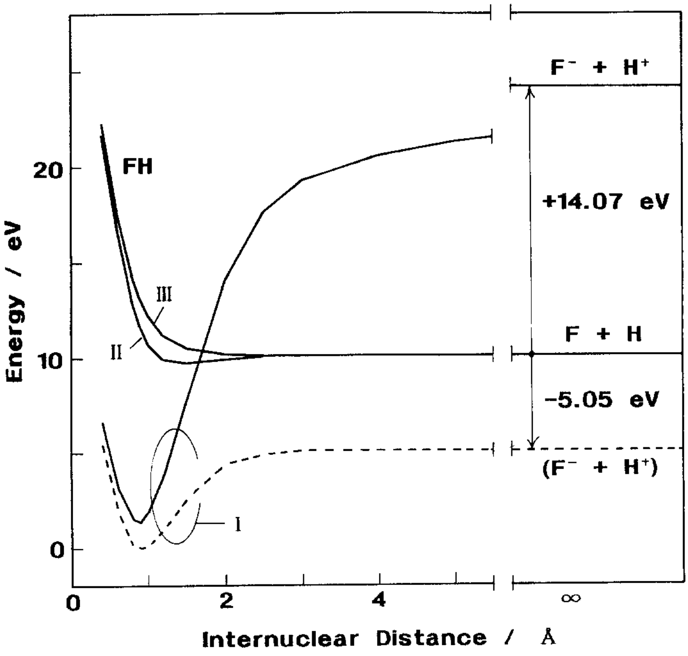

Fig. 6. Calculated potential energy curves for various configurations of FH. *Broken line*: $E_{J(0)}$; *solid line*: $E_{J(0)} + E_{J(1)AA} + E_{J(1)AB}$. I: [core] $(2\sigma)^2(3\sigma)^2(1\pi)^4$; II: [core] $(2\sigma)^2(3\sigma)^2(1\pi)^3(4\sigma)^1$; III: [core] $(2\sigma)^2(3\sigma)^1(1\pi)^4(4\sigma)^1$

As seen from Figs. 5 and 6, the differences between the zeroth-order energy curves and the first-order-corrected curves are not so large around the r_e. However, as internuclear distance increases, the first-order-corrected curves of configuration I become much higher than the zeroth-order curves, cross configurations II and III, and reach the final states of heterolytic dissociation ($As^+ + H^-$ and $F^- + H^+$). This is mainly due to the increase of the intracellular electronic repulsion ($E_{(1)AA}$) originating from the negatively charged atom (H in AsH and F in FH). On the other hand, both the zeroth-order and the first-order-corrected curves of configurations II and III reach the same energy level for the final states of homolytic dissociations (As + H and F + H). The energy levels for the final states of heterolytic dissociation calculated by the first-order approximation are roughly in agreement with the experimental data (9.06 eV for $As^+ + H^-$ and 16.67 eV for $F^- + H^+$) [6, 10], while the zeroth-order approximation fails to estimate even the sign of of the energy levels.

Finally, it should be noted that the potential energy curves, calculated by the first-order LEAF method, for the ground state and valence-shell-excited states of FH (Fig. 6) are semi-quantitatively consistent with those calculated by reliable CI methods, except for the singlet-triplet splitting and the configuration mixing between configurations I and III having the same spin and angular momentum [9]. This means that while the exact potential energy surfaces may need to be obtained by laborious calculations, the qualitative potential energy surfaces of the ground state and valence-shell-excited states of molecules can be predicted by the first-order LEAF method, which saves as much computer time and memory as EH methods.

5. Conclusions

The formula which describes an approximate relation between LEAF (or Wigner–Seitz-type) one-electron Hamiltonians and the complete Hamiltonian for a system (any molecule or solid) was derived (Eq. (25)). According to this formula, the complete Hamiltonian for a system is divided into four terms: the sum of LEAF one-electron Hamiltonians of all electrons in the system, the electronic repulsion originating from the charges of atomic cells, the Coulomb potential between charged cells, and a constant term.

It was shown that the approximate total energy for a system can be obtained from a first-order many-body perturbation theory in which the uperturbed term is the sum of LEAF one-electron Hamiltonians plus the constant term, and the perturbation is the remaining terms. The resultant total energy is approximately formulated as a quadratic function of the zeroth-order atomic charges added to the sum of the energies of occupied LEAF orbitals. For a molecule and a solid which have neither polarity nor charge, the total energy is approximately equal to the sum of occupied LEAF orbital energies plus the constant value. This approximate formula for total energy was found to justify the procedure for calculating the cohesive energies in the Wigner–Seitz method and the formula for total energy in the Hückel methods.

The r_es and the valence-shell excitation energies of diatomic molecules were calculated by the first-order formulation based on LEAF. These results show the soundness of the approximate relation between the LEAF one-electron Hamiltonians and the complete Hamiltonian for any system. The first-order correction, especially the electronic repulsion originating in the charge of each atomic cell, was shown to be important in calculations of r_e for GaH and of the potential energy curves of AsH and FH. An example of the intelligible analysis of the $E_{G(1)}$ curve in terms of cellular charges was shown for GaH. Finally, it was suggested that the first-order LEAF method could give at least qualitative potential energy surfaces for various electronic states of molecules without laborious calculations.

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Appendices

A1. Calculation of molecular orbitals and atomic cellular charges

When solving the eigenvalue problem as

$$\hat{h}(\mu)\phi = \varepsilon\phi, \tag{A1}$$

the following approximate LEAF Hamiltonian ($\hat{h}$) is adopted, assuming that each core atomic orbital (AO) does not overlap with either valence orbitals or other core AOs [4]. For the core orbitals in the αth cell (C_α) in a molecule or a solid,

$$\hat{h} \sim \sum_{\{\alpha nl\} \subset U_\alpha} e_{\alpha nl} \sum_{k \in \{\alpha nl\}} |\chi_k\rangle\langle\chi_k|, \tag{A2}$$

and for the valence orbitals in the system,

$$\hat{h} \sim \sum_{\alpha=1}^{N_n} \sum_{\{\alpha nl\} \subset V_\alpha} W_{\alpha nl} e_{\alpha nl} \sum_{k \in \{\alpha nl\}} |\chi_k\rangle\langle\chi_k|, \tag{A3}$$

where U_α and V_α denote the set of core AOs and that of valence AOs of the αth imaginary atom, respectively, $\{\alpha, n, l\}$ the set of AOs that belong to U_α or V_α and have both a principal number n and an azimuthal number l, $e_{\alpha nl}$ the orbital energy of the AOs that belong to $\{\alpha, n, l\}$, χ_k the kth AO in the system, and $W_{\alpha nl}$ (the integral of χ_k^2 in C_α, where $\chi_k \in \{\alpha, n, l\}$) is a function of overlap integrals as

$$W_{\alpha nl} \equiv \sum_{i \in \{\alpha nl\}} \sum_{j \in V_\alpha} |[S^{1/2}]_{ij}|^2/(2l+1). \tag{A4}$$

In Eq. (A4) $[M]_{ij}$ denotes the (i, j) element of the matrix M, and S the matrix of overlap integrals between AOs in the system. Here, it should be noted that the $W_{\alpha nl}$s decrease as the size of the system (the sum of cellular sizes) decreases. This represents the 'quantum size effect', i.e. the effect that the kinetic energy of an electron should increase as the wavelength of the orbital function decreases.

From approximation (A2), the eigenfunctions for core electrons in the system remain the core AOs in the isolated state. From approximation (A3), the eigenfunctions for valence electrons are the linear combination of valence AOs. Therefore, the ith eigenfunctions of Eq. (A1) can be represented as

$$\phi_i \sim \sum_{r \in \Omega} C_{ri}\chi_r, \tag{A5}$$

where Ω denotes all AOs in the system, and C_{ri} is the coefficient for the rth AO in ϕ_i, Thus, the matrix representation for Eq. (A1) is

$$(\boldsymbol{SWeS})\boldsymbol{C} = \boldsymbol{SC}\boldsymbol{\varepsilon}, \tag{A6}$$

where $\boldsymbol{W}$ denotes the diagonal matrix (elements of which are unities for core AOs and $W_{\alpha nl}$s for valence AOs), $\boldsymbol{e}$ the diagonal matrix of $\{e_{\alpha nl}\}$, $\boldsymbol{C}$ the matrix of $\{C_{ri}\}$, and $\boldsymbol{\varepsilon}$ the diagonal matrix of the molecular orbital energies $\{\varepsilon_i\}$.

In actual calculations, we estimated the charges of the cells ($Q_{J\alpha} \equiv \langle \Phi_{J(0)} | -K_\alpha | \Phi_{J(0)} \rangle$) by Mulliken's atomic population as

$$Q_{J\alpha} = Z_\alpha - \sum_{i=1}^{d} \sum_{r \in U_\alpha \cup V_\alpha} \sum_{s \in \Omega} v_i C_{ri} C_{si} S_{rs}. \tag{A7}$$

A2. Evaluation of atomic parameters

From Eqs. (28)–(31), the total energy of a free atom can be represented as

$$E_J = \sum_{\{\alpha nl\} \subset U_\alpha \cup V_\alpha} n_{\alpha nl} e_{\alpha nl} + (1/2) Q_{J\alpha}(Q_{J\alpha} - 1)\gamma_{\alpha v} + \text{const}, \tag{A8}$$

where $n_{\alpha nl}$ is the number of the electrons that occupy the AOs that belong to $\{\alpha, n, l\}$ (where $n_{\alpha nl} = 0, 1, \ldots, 4l + 2$). Let the first ionization potential that removes an electron from an AO that belongs to $\{\alpha, n, l\}$ be $I_1(\alpha, n, l)$, and let the second ionization potential that removes an electron from an AO that belongs to $\{\alpha, n, l\}$ be $I_2(\alpha, n, l)$. From Eq. (A8), one obtains

$$e_{\alpha nl} = -I_1(\alpha, n, l) \tag{A9}$$

and

$$\gamma_{\alpha v} = I_2(\alpha, n, l) - I_1(\alpha, n, l). \tag{A10}$$

Thus the atomic parameters ($e_{\alpha nl}$ and $\gamma_{\alpha v}$) can be evaluated from the experimental ionization potentials of free atoms. When evaluating the ionization potentials, we usually use the experimental energy levels of the most stable configurations for a given AO and given valency of the atom.

A3. Derivation of Wolfsberg–Helmholtz formula

From Eq. (A3), the matrix element between valence AOs is written as

$$\langle \chi_r | \hat{h} | \chi_s \rangle = \sum_k S_{rk} W_k e_k S_{ks}, \tag{A11}$$

where S_{rk} is the overlap integral between χ_r and χ_s, and W_k is $W_{\alpha nl}$ for χ_k. Replacing the W_ks with unities as well as neglecting the terms in which $|S_{rk}| < 1$ and $|S_{ks}| < 1$, one obtains a similar matrix element as a conventional EH (Wolfsberg–Helmholtz [8]) formula, i.e.

$$\langle \chi_r | \hat{h}_{\text{WH}} | \chi_s \rangle = \begin{cases} e_r & (r = s) \\ (1/2) K S_{rs}(e_r + e_s) & (r \neq s), \end{cases} \tag{A12}$$

where K denotes the constant parameter. However, the lack of the variable W_k which could represent the 'quantum size effect' is fatal for bond-length calculations.

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