

Variational principles which are functionals of electron density*

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The Ritz variational principle, ordinarily written as a functional of the ground-state wavefunction, is rewritten in such a way that only one-electron functions are included as variables. Three different such variational formulas are derived explicitly based on the formula given by Hohenberg and Kohn. They constitute variational expressions of the integrated Hellmann–Feynman theorem, integral Hellmann–Feynman theorem, and virial theorem. These variational formulas are exact within the Born–Oppenheimer approximation, and when applied, they give the same results as does the conventional Ritz variational principle. However, they still have the defect that they require knowledge of the correct density function associated with a suitably chosen reference potential. Some applications are given for one-electron systems. A new formula for the kinetic energy plus electron–electron repulsion energy is obtained from the integrated Hellmann–Feynman theorem.

I. INTRODUCTION

Electron density, which describes the three dimensional distribution of electrons in a system, is one of the most fundamental observables in quantum mechanics. Because of its physical perspicuity, it is highly desirable to try to use this quantity as a basic variable in quantum chemistry. The statistical models of atomic and molecular structures, such as the Thomas–Fermi model and its various extensions,¹ belong to this kind of approach. However, they are crude approximations for the actual atomic and molecular electronic structures.^{2,3}

The ordinary Ritz variational principle states that the exact ground-state energy E is always a lower bound for the energy functional of a trial wavefunction Ψ' ; $E \leq \bar{E}[\Psi']$. For the density approach, the first question concerns the existence of a variational principle as a functional of electron density; $E \leq \bar{E}[\rho']$. A decade ago, Hohenberg and Kohn⁴ showed formally that such variational principles exist, but they did not give any explicit operational formula. The purpose of the present paper is to give explicitly several exact operational formulas for such variational principles.

There already exist three relations between the exact energy and exact density functions (electron density, transition density, etc.), the integrated form of the Hellmann–Feynman theorem⁵ [or the integrated Hellmann–Feynman (IdHF) theorem⁶], the integral Hellmann–Feynman (IHF) theorem,⁷ and the virial theorem.⁸ However, the energies given by these theorems are not stationary to small variations in the density functions involved.

We first briefly develop the idea of Hohenberg and Kohn.⁴ Then we derive, using the energy and density relations given by the IdHF, IHF, and virial theorems, three different exact variational formulas which include only one-electron functions as variables. We show that when these formulas are applied, they give the same results as does the ordinary Ritz variational principle. Finally we make some general remarks.

II. VARIATIONAL PRINCIPLES

We consider a nondegenerate ground state of an N -electron system within the Born–Oppenheimer approximation. The electronic Hamiltonian is written as

$$\mathcal{H} = \mathcal{T} + \mathcal{V}_{ee} + \mathcal{V}_{ne}(\alpha) \quad (1)$$

where \mathcal{T} is the electron kinetic operator, $\mathcal{T} = \sum_{\mu}^N - (1/2)\Delta_{\mu}$, and \mathcal{V}_{ee} the electron–electron repulsion operator, $\mathcal{V}_{ee} = \sum_{\mu < \nu}^N 1/r_{\mu\nu}$. The term $\mathcal{V}_{ne}(\alpha)$ represents the external potential composed of one-electron operators. It defines the system under consideration, i. e., all of the necessary information about the system is included in the functional form of v and a set of parameters $\alpha = \{\alpha_i\}$ in the expression

$$\mathcal{V}_{ne}(\alpha) = \sum_{\mu}^N v(\mathbf{r}_{\mu}; \alpha) \quad (2)$$

For atomic and molecular systems, v denotes the electrostatic electron–nuclear attraction potential

$$v(\mathbf{r}; \alpha) = v(\mathbf{r}; \mathbf{R}_A, \mathbf{R}_B, \dots, \mathbf{R}_M, Z_A, Z_B, \dots, Z_M) \\ = - \sum_A^M Z_A / |\mathbf{r} - \mathbf{R}_A| \quad (3)$$

and the parameters $\{\alpha_i\}$ represent the nuclear coordinates \mathbf{R}_A and atomic numbers Z_A . The Schrödinger equation, $\mathcal{H}(\alpha)\Psi(\alpha) = E(\alpha)\Psi(\alpha)$, defines the ground state $\Psi(\alpha)$ and the exact energy $E(\alpha)$. The electron density of the state is defined by

$$\rho(\mathbf{r}; \alpha) = N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \alpha) \\ \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \alpha) d\mathbf{s}_2 \cdots d\mathbf{x}_N \\ = N \langle \Psi(\alpha) | \Psi(\alpha) \rangle_1 \quad (4)$$

The variable \mathbf{x} denotes both spin (\mathbf{s}) and space (\mathbf{r}) coordinates.

Now, we introduce an N -electron reference Hamiltonian \mathcal{H}' ,

$$\mathcal{H}'(\beta) = \mathcal{T} + \mathcal{V}_{ee} + \mathcal{V}'_{ne}(\beta) \quad (5)$$

which differs from the exact Hamiltonian \mathcal{K} of Eq. (1) only in the external potential term,

$$v'_{ne}(\beta) = \sum_{\mu}^N v'(\mathbf{r}_{\mu}; \beta) . \quad (6)$$

We refer to $v'_{ne}(\beta)$ and $v'(\mathbf{r}; \beta)$ as reference potentials. The associated ground-state wavefunction and electron density are denoted by $\Psi'(\beta)$ and $\rho'(\mathbf{r}; \beta)$. From the Ritz variational principle, we obtain

$$\begin{aligned} \langle \Psi | \mathcal{K} | \Psi \rangle &\leq \langle \Psi' | \mathcal{K} | \Psi' \rangle \\ &= \langle \Psi' | \mathcal{K}' + v'_{ne}(\alpha) - v'_{ne}(\beta) | \Psi' \rangle , \end{aligned} \quad (7)$$

or

$$\begin{aligned} E(\alpha) &\leq \bar{E}(\beta) \\ &= E'(\beta) + \int d\mathbf{r} \rho'(\mathbf{r}; \beta) [v(\mathbf{r}; \alpha) - v'(\mathbf{r}; \beta)] , \end{aligned} \quad (8)$$

where $\bar{E}(\beta)$ is the approximate energy for the exact Hamiltonian, $\bar{E}(\beta) = \langle \Psi' | \mathcal{K} | \Psi' \rangle$, and $E'(\beta)$ is the correct energy associated with the reference Hamiltonian $\mathcal{K}'(\beta)$. If we denote the sum of the kinetic and electron-electron repulsion energies for $\mathcal{K}'(\beta)$ as $F'(\beta)$, Eq. (8) may be rewritten as

$$E(\alpha) \leq \bar{E}(\beta) = F'(\beta) + \int d\mathbf{r} \rho'(\mathbf{r}; \beta) v(\mathbf{r}; \alpha) . \quad (9)$$

We will soon understand that some of the parameters $\beta = \{\beta_i\}$ are essentially the variational parameters.

Equations (8) and (9) were first derived by Hohenberg and Kohn and used to prove the existence of the variational principle as a functional of electron density.⁴ Their claim is correct and it can be realized and extended more explicitly. Since the energy $E'(\beta)$ is defined as the *correct* energy associated with the reference potential v' , we can use the IdHF, IHF, and virial theorems for $E'(\beta)$ and express the variational formula (8) explicitly in a form which includes only one-electron functions as variables.

A. Variational IdHF formula

The integrated Hellmann-Feynman (IdHF) theorem⁶ is given by⁹

$$\Delta E(\alpha) = \int_{\alpha_0}^{\alpha} d\alpha' \int d\mathbf{r} \rho(\mathbf{r}; \alpha') \frac{\partial v(\mathbf{r}; \alpha')}{\partial \alpha'} , \quad (10)$$

where $\Delta E(\alpha) = E(\alpha) - E(\alpha_0)$. This means that if we know the electron density along the isoelectronic path $\alpha_0 - \alpha$, we can calculate the exact energy difference $\Delta E(\alpha)$. When we write all the nuclear charges as $Z_A = z Z_A$ and consider the hypothetical change from $z = 0$ to $z = 1$, Eq. (10) reduces to the Wilson formula,¹⁰ which gives the absolute energy of the system^{11,12}

$$E(\alpha) = \int_{z=0}^1 dz \int d\mathbf{r} \rho(\mathbf{r}; \alpha) \frac{\partial v(\mathbf{r}; \alpha)}{\partial z} . \quad (11)$$

Integrating the IdHF formula by parts with respect to $d\alpha$, we can derive a new separate formula for the change in kinetic energy plus electron-electron repulsion energy, $F = T + V_{ee}$, as

$$\Delta F = - \int_{\alpha_0}^{\alpha} d\alpha' \int d\mathbf{r} \frac{\partial \rho(\mathbf{r}; \alpha')}{\partial \alpha'} v(\mathbf{r}; \alpha') . \quad (12)$$

This corresponds to an explicit expression of the functional $F[\rho]$ introduced by Hohenberg and Kohn. When we take nuclear coordinates as α , this equation will provide a new picture of chemical bond formation. The concepts of electron-cloud following and preceding,¹³ which were pointed out previously to be very useful for understanding molecular structure, molecular vibrations, and chemical reactions,^{14,15} are concepts related with the derivative, $\partial \rho / \partial \alpha$.

Now we derive the variational expression of the IdHF formula. First, we assume that the reference potential $v'(\mathbf{r}; \beta)$ coincides with the exact potential $v(\mathbf{r}; \alpha)$ at some appropriately chosen initial states β_0 and α_0 ,

$$v'(\mathbf{r}; \beta_0) = v(\mathbf{r}; \alpha_0) . \quad (13)$$

Then $E(\alpha_0) = E'(\beta_0)$. Inserting the IdHF formula for the reference energy into Eq. (8), we obtain

$$\begin{aligned} \Delta E(\alpha) \leq \Delta \bar{E}(\beta) &= \int_{\beta_0}^{\beta} d\beta' \int d\mathbf{r} \rho'(\mathbf{r}; \beta') \frac{\partial v'(\mathbf{r}; \beta')}{\partial \beta'} \\ &+ \int d\mathbf{r} \rho'(\mathbf{r}; \beta) [v(\mathbf{r}; \alpha) - v'(\mathbf{r}; \beta)] . \end{aligned} \quad (14)$$

Similarly, from Eqs. (9) and (12), we obtain

$$\begin{aligned} \Delta E(\alpha) \leq \bar{E}(\beta) &= - \int_{\beta_0}^{\beta} d\beta' \int d\mathbf{r} \frac{\partial \rho'(\mathbf{r}; \beta')}{\partial \beta'} v'(\mathbf{r}; \beta') \\ &+ \int d\mathbf{r} \rho'(\mathbf{r}; \beta) v(\mathbf{r}; \alpha) \\ &- \int d\mathbf{r} \rho'(\mathbf{r}; \beta_0) v(\mathbf{r}; \alpha_0) . \end{aligned} \quad (15)$$

Equations (14) and (15) are equivalent and constitute the variational expression of the IdHF formula. They include only one-electron functions as variables. In these equations, the choice of the reference potential v' is arbitrary except for Eq. (13). Its arbitrariness may guarantee the arbitrariness of the associated density ρ' . The correspondence between v' and ρ' is unique as shown by Hohenberg and Kohn. The exact energy $\Delta E(\alpha)$ is always a lower bound for any associated variations in v' and ρ' . When applied to actual systems, these variational formulas give the same results as does the ordinary Ritz variational principle (see examples). For $v' = v$, these formulas reduce to the original IdHF formulas (10) and (12). In Eq. (15), the first term corresponds to the sum of the kinetic and electron-electron repulsion energies and the last two terms to the electron-nuclear attraction energy, but in Eq. (14), such a correspondence does not exist. We may suppose that the trial density ρ' is N -representable¹⁶ in this formulation.

Although the variational formulas (14) and (15) are formally exact, they still have a defect in general applicability. We have to know the correct density ρ' associated with the reference potential v' . However, we don't have available any way, at present, to calculate ρ' except by solving the Schrödinger equation for the reference Hamiltonian $\mathcal{K}'(\beta)$! The reference Hamiltonian $\mathcal{K}'(\beta)$ includes the same two-electron interaction

part v_{ee} as does the exact Hamiltonian $\mathcal{H}(\alpha)$, and a possible simplification in the one-electron potential v' does not necessarily help much the solution of the Schrödinger equation for the reference Hamiltonian. It can be as hard as solving the exact Schrödinger equation, $\mathcal{H}(\alpha)\Psi(\alpha) = E(\alpha)\Psi(\alpha)$.

An important exception to this is the case of the harmonic reference potential. Kestner and Sinanoglu¹⁷ have shown that the Schrödinger equation for the two-electron model Hamiltonian

$$\mathcal{H}'(\beta) = -\frac{1}{2}(\Delta_1 + \Delta_2) + \frac{1}{2}\beta^2(r_1^2 + r_2^2) + 1/r_{12} \quad (16)$$

can be solved exactly and studied the electron-correlation effect in this model system.

B. Variational IHF formula

The integral Hellmann-Feynman (IHF) theorem⁷ is written as

$$\Delta E(\alpha) = \int d\mathbf{r} \tau(\mathbf{r}; \alpha_0, \alpha) [v(\mathbf{r}; \alpha) - v(\mathbf{r}; \alpha_0)] \quad (17)$$

where $\tau(\mathbf{r}; \alpha_0, \alpha)$ is the normalized transition density, defined by

$$\tau(\mathbf{r}; \alpha_0, \alpha) = \frac{N}{S} \langle \Psi(\alpha_0) | \Psi(\alpha) \rangle_1 \quad (18)$$

The quantity S is the overlap integral between the initial (α_0) and final (α) states,

$$S = \langle \Psi(\alpha_0) | \Psi(\alpha) \rangle \quad (19)$$

The nature of the IHF theorem has been well investigated.^{6,7}

In order to calculate the absolute energy of the system from the IHF formula, we may use the wavefunction for the state in which $v(\mathbf{r}; \alpha_0) = 0$, i. e., the zero-energy state

$$H(0)\Psi(0) = 0 \quad (20)$$

where $H(0)$ is given by

$$H(0) = \mathcal{T} + v_{ee} \quad (21)$$

For one-electron systems, $\Psi(0)$ may be written in unnormalized form as

$$\Psi(0) = 1 \quad (22)$$

while for two-electron systems, it may be written as

$$\Psi(0) = \sum_{n=0}^{\infty} r_{12}^n / n!(n+1)! \quad (23)$$

Both Eqs. (22) and (23) satisfy Eq. (20).⁶

The variational expression of the IHF theorem may be derived by a method similar to that used for the IdHF case. We again assume Eq. (13) and obtain the result

$$\Delta E(\alpha) \leq \Delta \bar{E}(\beta) = \int d\mathbf{r} \tau'(\mathbf{r}; \beta_0, \beta) [v'(\mathbf{r}; \beta) - v(\mathbf{r}; \alpha_0)] - \int d\mathbf{r} \rho'(\mathbf{r}; \beta) [v'(\mathbf{r}; \beta) - v(\mathbf{r}; \alpha)] \quad (24)$$

Here, τ' is the correct transition density associated with the reference potential v' . In contrast with the IdHF case, this formula does not require knowledge of ρ' over the whole range $\beta_0 \rightarrow \beta$, but it does require the two quantities, ρ' and τ' , at the final state β . In use of Eq. (24), the point $\beta = \beta_0$ must be excluded from the variational domain, since $\Psi(0)$ is not square integrable.

C. Variational virial formula

The quantum-mechanical virial theorem also provides a relationship between the energy and the density function of the system. However, this theorem is restrictive in that all the potentials of the system are presumed to have the form of the electrostatic Coulomb potential, i. e., to be linear in the inverses of the interparticle distances. For polyatomic molecules, the theorem may be written⁸

$$2T + V_{ee} + V_{ne} + \sum_A \mathbf{R}_A \cdot \frac{\partial E}{\partial \mathbf{R}_A} = 0 \quad (25)$$

where the derivative $\partial E / \partial \mathbf{R}_A$ means a vector

$$\left(\frac{\partial E}{\partial X_A}, \frac{\partial E}{\partial Y_A}, \frac{\partial E}{\partial Z_A} \right)$$

Using the Hellmann-Feynman theorem

$$\frac{\partial E}{\partial \mathbf{R}_A} = \int d\mathbf{r} \rho(\mathbf{r}; \alpha) \frac{\partial v(\mathbf{r}; \alpha)}{\partial \mathbf{R}_A} \quad (26)$$

and the relation $E = T + V_{ee} + V_{ne}$, we can rewrite the virial theorem in the form

$$E(\alpha) = \frac{1}{2} \int d\mathbf{r} [\Delta(\mathbf{r}') \rho(\mathbf{r}, \mathbf{r}'; \alpha)]_{\mathbf{r}' = \mathbf{r}} - \sum_A \mathbf{R}_A \int d\mathbf{r} \rho(\mathbf{r}; \alpha) \frac{\partial v(\mathbf{r}; \alpha)}{\partial \mathbf{R}_A} \quad (27)$$

where $\rho(\mathbf{r}, \mathbf{r}'; \alpha)$ is the first-order density matrix.¹⁸ Its diagonal element is the electron density, $\rho(\mathbf{r}; \alpha)$. This theorem requires knowledge of both $\rho(\mathbf{r}; \alpha)$ and $\rho(\mathbf{r}, \mathbf{r}'; \alpha)$.

The variational expression associated with the virial theorem is found to be

$$E(\alpha) \leq \bar{E}(\beta) = \frac{1}{2} \int d\mathbf{r} [\Delta(\mathbf{r}') \rho'(\mathbf{r}, \mathbf{r}'; \beta)]_{\mathbf{r}' = \mathbf{r}} - \sum_A \mathbf{R}'_A \int d\mathbf{r} \rho'(\mathbf{r}; \beta) \frac{\partial v'(\mathbf{r}; \beta)}{\partial \mathbf{R}'_A} + \int d\mathbf{r} \rho'(\mathbf{r}; \beta) [v(\mathbf{r}; \alpha) - v'(\mathbf{r}; \beta)] \quad (28)$$

where $\rho'(\mathbf{r}; \beta)$ and $\rho'(\mathbf{r}, \mathbf{r}'; \beta)$ are the correct density functions associated with the reference potential v' , and the quantities \mathbf{R}'_A are the nuclear coordinates chosen in the reference potential v' .

Note that in the variational formula (28), the choice of the reference potential is not quite arbitrary but is restricted to have the form of an electrostatic potential. In comparison with the IdHF and IHF cases, the varia-

tional virial formula therefore is more limited in applicability.

III. ILLUSTRATIVE APPLICATIONS

In this section, we give some applications of the variational formulas given above. Owing to the difficulties already stated, we limit ourselves to one-electron problems. They are the Z dependence of the electron density of one-electron atom, and the single Gaussian orbital approximations for one-electron atoms and for H_2^+ .

A. Z dependence

The electron density of the ground state of the one-electron atom with nuclear charge Z is given by the formula

$$\rho(r; Z) = (Z^3/\pi) \exp(-2Zr). \quad (29)$$

The associated potential is

$$v(r; Z) = -Z/r. \quad (30)$$

We suppose that we don't know the Z dependence of the electron density, and we choose as a trial density

$$\rho'(r; Z, n) = N \exp(-2Z^n r), \quad (31)$$

where n is a variational parameter. From the normalization condition, $N = Z^{3n}/\pi$. The reference potential associated with $\rho'(r; Z, n)$ is

$$v'(r; Z, n) = -Z^n/r. \quad (32)$$

As an initial state, we could choose $Z_0 = 0$, $Z_0 = 1$, or $n_0 = 1$; all of these states satisfy Eq. (13). Here we choose $Z_0 = 0$ as our initial state. Hence $E(Z=0) = 0$.

First we apply the variational expression of the IdHF energy. Inserting the above quantities into Eqs. (14) and (15), we obtain

$$E(Z) \leq \bar{E}(Z, n) = \frac{1}{\pi} \int_0^Z dZ' \int d\mathbf{r} Z'^{3n} \exp(-2Z'^n r) \frac{\partial}{\partial Z'} \left(-\frac{Z'^n}{r} \right) + \frac{Z^{3n}}{\pi} \int d\mathbf{r} \left[-\frac{Z}{r} + \frac{Z^n}{r} \right] \exp(-2Z^n r), \quad (33)$$

and

$$E(Z) \leq \bar{E}(Z, n) = -\frac{1}{\pi} \int_0^Z dZ' \int d\mathbf{r} \left(-\frac{Z'^n}{r} \right) \times \frac{\partial}{\partial Z'} \{ Z'^{3n} \exp(-2Z'^n r) \} + \frac{Z^{3n}}{\pi} \int d\mathbf{r} \left(-\frac{Z}{r} \right) \exp(-2Z^n r), \quad (34)$$

respectively. After integration, both reduce to

$$\bar{E}(Z, n) = \frac{1}{2} Z^{2n} - Z^{n+1}; \quad \frac{\partial \bar{E}(Z, n)}{\partial n} = (Z^{2n} - Z^{n+1}) \log Z. \quad (35)$$

The condition $\partial \bar{E}(Z, n)/\partial n = 0$ gives $Z = 1$ or $n = 1$. The former corresponds to the hydrogen atom case and the latter gives the correct Z dependence as seen in Eq. (29). The best energy is thus $\bar{E}(n=1) = -(1/2)Z^2$, which is the exact energy of the one-electron atom. Note that the first integral of the rhs of Eq. (34) gives the exact kinetic energy $(1/2)Z^2$ when $n=1$, as it should.

Secondly, we apply the variational IHF formula (24). The transition density τ' is obtained from Eq. (22) as

$$\tau'(r; 0, Z) = \frac{Z^{3n}}{8\pi} \exp(-Z^n r). \quad (36)$$

Thus Eq. (24) becomes

$$E \leq \bar{E}(n) = \frac{1}{8\pi} Z^{3n} \int d\mathbf{r} (-Z^n/r) \exp(-Z^n r) - \frac{1}{\pi} Z^{3n} \int d\mathbf{r} (-Z^n/r + Z/r) \exp(-2Z^n r) = \frac{1}{2} Z^{2n} - Z^{n+1}. \quad (37)$$

This is identical with Eq. (35). The minimum condition therefore gives the same correct Z dependence, $n=1$, and the exact energy, $-(1/2)Z^2$.

Lastly, we test the variational virial formula. The quantity $\rho'(r, r'; \beta)$ is written down as

$$\rho'(r, r'; Z, n) = \left(\frac{Z^{3n}}{\pi} \right) \exp[-Z^n(r+r')]. \quad (38)$$

The second term of the rhs of Eq. (28) vanishes for this system. Then, Eq. (28) becomes, after some manipulations,

$$E \leq \bar{E}(n) = \frac{Z^{3n}}{\pi} \int d\mathbf{r} (Z^{2n}/2 - Z^n/r) \exp(-2Z^n r) + \frac{Z^{3n}}{\pi} \int d\mathbf{r} (-Z/r + Z^n/r) \exp(-2Z^n r) = \frac{1}{2} Z^{2n} - Z^{n+1}. \quad (39)$$

This is again identical with Eq. (35). The minimum condition gives the correct Z dependence, $n=1$, and the exact energy, $-(1/2)Z^2$.

Note that the integrands of Eqs. (33), (34), (37), and (39) are all different even when $n=1$. These integrands might be called "energy densities," since their integration over the whole three dimensional space gives the energy of the system. A similar ambiguity of the energy density will also be seen in the applications below.

B. Single Gaussian orbital-harmonic potential

We may approximate the ground state of a one-electron atom by a single Gaussian orbital

$$\Psi' = (\beta/\pi)^{3/4} \exp(-\frac{1}{2}\beta r^2). \quad (40)$$

Since Ψ' is an eigenfunction for the harmonic potential

$$v'(r, \beta) = \frac{1}{2} \beta^2 r^2, \quad (41)$$

this approximation corresponds to taking a harmonic potential as a reference potential. Note that the variational virial formula cannot be applied to this model, because the potential (41) is not an electrostatic potential.

First, we apply the variational IdHF formula. As an initial state, we choose the state $\beta_0 = 0$ for the reference potential and $Z_0 = 0$ for the exact potential, so that they satisfy Eq. (13). The trial density is just the square of Eq. (40). The variational formula (15) thus becomes

$$E \leq \bar{E}(\beta) = -\left(\frac{1}{\pi}\right)^{3/2} \int_0^\beta d\beta' \int d\mathbf{r} \frac{1}{2} \beta'^2 r^2 \frac{\partial}{\partial \beta'} \times [\beta'^{3/2} \exp(-\beta' r^2)]$$

$$\begin{aligned}
 & + \left(\frac{\beta}{\pi}\right)^{3/2} \int dr (-Z/r) \exp(-\beta r^2) \\
 & = \frac{3}{4} \beta - 2 \left(\frac{\beta}{\pi}\right)^{1/2} Z .
 \end{aligned} \tag{42}$$

The minimum condition gives the best values of β as $\beta_{\text{best}} = (16/9\pi) Z^2$ and the best variational energy as $\bar{E}(\beta_{\text{best}}) = -(4/3\pi) Z^2 = -0.424 Z^2$. This is 85% of the exact energy, $-(1/2)Z^2 = -0.5 Z^2$. The second derivative of $\bar{E}(\beta)$ shows that this corresponds to the true minimum. Note that the first term of Eq. (42), which is the kinetic energy part, gives the value $(4/3\pi)Z^2$. Thus the virial theorem holds. These results are identical with those of the conventional Ritz variational principle.⁶

Next, we use the variational IHF formula. The normalized transition density is obtained as

$$\tau'(r; 0, \beta) = \left(\frac{\beta}{2\pi}\right)^{3/2} \exp(-\frac{1}{2}\beta r^2) . \tag{43}$$

Then, Eq. (24) becomes

$$E \leq \bar{E}(\beta) = \left(\frac{\beta}{2\pi}\right)^{3/2} \int dr (\frac{1}{2}\beta^2 r^2) \exp(-\frac{1}{2}\beta r^2)$$

$$E \leq \bar{E}(\beta, R) = -\left(\frac{1}{\pi}\right)^{3/2} \int_0^\beta d\beta' \int dr (\frac{1}{2}\beta'^2 r^2) \frac{\partial}{\partial \beta'} [\beta'^{3/2} \exp(-\beta' r^2)] + \left(\frac{\beta}{\pi}\right)^{3/2} \int dr \left[\frac{-Z}{|r-R|} + \frac{-Z}{|r+R|} \right] \exp(-\beta r^2) , \tag{46}$$

which reduces to¹⁹

$$E \leq \bar{E}(\beta, R) = \frac{3}{4} \beta - \frac{2Z}{R} \text{erf}(R\sqrt{\beta}) , \tag{47}$$

where $\text{erf}(t)$ stands for the error function

$$\text{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-u^2) du . \tag{48}$$

The total energy of the system is the sum of the electronic energy and the nuclear-nuclear repulsion energy:

$$W \leq \bar{W}(\beta, R) = \frac{3}{4} \beta - \frac{2Z}{R} \text{erf}(R\sqrt{\beta}) + \frac{Z^2}{2R} . \tag{49}$$

The best value of β and the theoretical estimate of the internuclear distance $2R_0$ are calculated from the conditions

$$\frac{\partial \bar{W}(\beta, R)}{\partial \beta} = 0; \quad \frac{\partial \bar{W}(\beta, R)}{\partial R} = 0 , \tag{50}$$

which gives $\beta_{\text{best}} = 0.635$, $2R_0 = 1.932$ a.u.²⁰ The experimental distance is 2.00 a.u. The variational energy at $R = R_0$ is 84% of the experimental value (-0.603 a.u.) and the calculated dissociation energy is 79% of the experimental value (-0.1026 a.u.). The variational IHF formula and the ordinary Ritz variational method²⁰ also give the same results.

IV. CONCLUDING REMARKS

In this paper we have sought to express the variational principle as a functional of only one-electron functions. Based on a formula given by Hohenberg and Kohn, three explicit expressions of such variational

$$\begin{aligned}
 & - \left(\frac{\beta}{\pi}\right)^{3/2} \int dr (\frac{1}{2}\beta^2 r^2 + Z/r) \exp(-\beta r^2) \\
 & = \frac{3}{4} \beta - 2 \left(\frac{\beta}{\pi}\right)^{1/2} Z ,
 \end{aligned} \tag{44}$$

which is identical with Eq. (42). Thus, both of the variational IdHF and IHF formulas give the same answer as does the ordinary Ritz variational principle.

C. Harmonic potential as a model of H_2^+

Here, we approximate the ground state of the hydrogen molecule-ion by the single Gaussian orbital [Eq. (40)] centered at the origin of coordinates. The reference potential is the harmonic potential given by Eq. (41). The two protons are placed along the x axis apart by distance R from the origin, $2R$ being the internuclear distance. The exact potential is then given by

$$v(r; Z, R) = -Z/|r-R| - Z/|r+R| , \tag{45}$$

where $R = (R, 0, 0)$.

First, we apply the variational IdHF formula. As in a preceding example, Eq. (15) is rewritten as

formulas have been derived from the energy and density relationships provided by the IdHF, IHF, and virial theorems. They are exact within the Born-Oppenheimer approximation, and when applied, they give the same results as does the conventional Ritz variational method. Although the original IdHF, IHF, and virial energy formulas are not stationary to small changes in the one-electron functions included, the equations we have given are stationary to such changes. For exact one-electron functions, they reduce to the original IdHF, IHF, and virial theorems.

The problem of the present variational formulas is that they require the correct density functions associated with an arbitrarily chosen reference potential. This is impossible to have, in general, for many-electron systems, except for some harmonic potentials.¹⁷ If we had a method for obtaining the potential v' associated with an arbitrarily chosen trial density ρ' , we could eliminate the reference potential v' from our expressions. Although there is no such method available, at present,²¹ even an approximate method could be very helpful. In developing an approximate method, it would be necessary to pay due attention to the problem of N -representability.¹⁶ Trial density functions should be restricted to those which are N -representable.

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$$\int_{z=0}^1 dz$$

may be understood as

$$\lim_{\epsilon \rightarrow 0} \int_{z=\epsilon}^1 dz.$$

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