$$+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|}\,.$$

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BH, CH, and CO, however, indicate that force and kinetic energy are not effective in yielding good dipole moments. These molecules are in a different class than the ones we report, in that they are generally considered to be more covalent in nature. There seems to be some significance to this, but any detailed analysis at the present time would be premature.

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Direct Determination of Pure-State Density Matrices. III.
Purely Theoretical Densities Via an Electrostatic-Virial Theorem*

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A combined electrostatic virial theorem is introduced and used to derive a differential equation for the scale factor ζ in a diatomic molecule. This equation can either be used to compute $d\zeta/dR$ or it can be integrated to yield

$$\zeta(\overline{R}) = \left(\frac{T(\overline{R}_0)}{T(\overline{R})}\right)^{1/2}\left(\zeta(\overline{R}_0) - \frac{1}{2T(\overline{R}_0)}\int_{\overline{R}}^{\overline{R}_0}\frac{2F(R) - RdF(R)/dR}{T(R)^{1/2}}\,dR\right),$$

where R is the internuclear distance, $\overline{R}\equiv\zeta R$, $F = \langle -\partial V_1/\partial R\rangle$, with V_1 the one-electron potential, $T\equiv\langle\sum_i -\frac{1}{2}\nabla_i^2\rangle$, and $\overline{R}_0$ is an integration limit. It is shown that if $\zeta(\overline{R}_0)$ is a variational scale factor, then $\zeta(\overline{R})$ is also a variational scale factor provided the electron density ρ_1 involves no other unoptomized variational parameters. Unlike the conventional variational expression for ζ, which contains two-electron integrals, the above formula involves only the one-electron force and kinetic energy integrals. Using this ζ, electron densities and energies are calculated for H_2^+, H_2, He_2, and Li_2 and compared with experimental and variationally calculated values. Qualitative agreement is obtained in general, and, in particular, our theoretical energy curve for He_2 is in very good agreement with the best variational results for 1.5 a.u. $< R < \infty$. It is also shown how the electrostatic-virial theorem can be used as a condition in continuing density-matirx calculations from R to $R+\Delta R$.

I. INTRODUCTION

In the first paper in this series,[1] the electrostatic and virial theorems were used to determine a semiempirical electron density. The method consisted of three main steps: (a) A simple functional form for $\rho_1(\vec{r}',\vec{r},R)$ was assumed and inserted into the electrostatic and virial theorems. (b) In place of the electronic energy $E(R)$ and its derivative $dE(R)/dR$, experimental data were used. (c) The resulting equations, which by virtue of (a) and (b) uniquely determine ρ_1, were solved.

In the present paper, a similar approach is followed except that the semiempirical aspect [step (b) above] is eliminated. This is accomplished by combining the electrostatic and virial theorems into a single equation that can be expressed entirely in terms of the one-body density $\rho_1(\vec{r}',\vec{r},R)$. This electrostatic-virial (EV) theorem can then be used as a purely theoretical condition on the one-body density.

If the density is expressed as $\rho_1 = \zeta^3\rho_1(\zeta\vec{r}', \zeta\vec{r}, \zeta R)$, the EV theorem serves to uniquely determine ζ in terms of force and kinetic-energy integrals involving only the unscaled density $\rho_1(\vec{r}', \vec{r}, R)$. In the first parts of this paper, a method is developed for the theoretical calculation of the scale factor ζ. It is shown that our ζ is the same as the variational scale factor provided the density contains no other unoptimized variational parameters. It is also shown computationally that, even though many of the densities we work with do contain other unoptimized variational parameters, our ζ's are, in every case, in qualitative agreement with the variational ζ's, and in one important case quantitative agreement is obtained.

The last part of the present paper is devoted to the derivation of density-matrix equations that allow one to continue an idempotent matrix from one value of a parameter λ to another $\lambda + \Delta\lambda$.

When $\lambda \equiv R$, the EV theorem can be used as a constraining condition in these equations.

II. COMBINED ELECTROSTATIC-VIRIAL THEOREM

Consider the electrostatic and virial theorems for a diatomic molecule. We have

$$(d/dR)E(R) = \int (\partial V_1/\partial R)\rho_1(\vec{r}, R)d^3r,$$
$$R(d/dR)E(R) + E(R) = -T(R)$$
$$\equiv \tfrac{1}{2}\int [\nabla^2\rho_1(\vec{r}', \vec{r}, R)]_{\vec{r}'=\vec{r}}\, d^3r, \qquad (1)$$

where V_1 is the one-body potential, R is the internuclear distance, and $E(R)$ is the electronic energy. We now define the electronic force as $F(R) \equiv -dE(R)/dR$. Differentiating the second of Eqs. (1) and using the definition of $F(R)$, we have

$$R\, dF(R)/dR + 2F(R) = dT(R)/dR. \qquad (2)$$

Equation (2) is the EV theorem referred to in Sec. I. It is an integrodifferential equation representing a necessary condition on an exact electron density. There are infinitely many densities which will satisfy Eq. (2). However, as demonstrated below, this infinity can be reduced to a single density by suitable choice of the functional form of $\rho_1(\vec{r}', \vec{r}, R)$. One such choice that is completely general involves the scaling of a known density. This is discussed next.

III. THE ELECTROSTATIC-VIRIAL EXPRESSION FOR THE SCALE FACTOR

We now consider a scaled first-order density $\zeta^3\rho_1(\zeta\vec{r}', \zeta\vec{r}, \zeta R)$ where $\rho_1(\vec{r}', \vec{r}, R)$ is known and is such that

$$\int \rho_1(\vec{r}, R)d^3r = N,$$

the total number of electrons. It then follows that $\zeta^3\rho_1(\zeta\vec{r}, \zeta R)$ also integrates to N. That is, letting $\vec{\bar{r}} \equiv \zeta\vec{r}$ and $\bar{R} \equiv \zeta R$ we have

$$\zeta^3 \int \rho_1(\vec{\bar{r}}, \bar{R})d^3r = \int \rho_1(\vec{\bar{r}}, \bar{R})d^3\bar{r} = N.$$

We now insert this density (and the corresponding kernel) into Eq. (2) in order to determine $\zeta(R)$. It is easily shown using dimensional arguments that

$$T(\zeta, R) \equiv \zeta^2 T(1, \bar{R}),$$

where $T(\zeta, R)$ is the kinetic energy for the scaled density at the internuclear distance R. One can also show that[2]

$$F(\zeta, R) = \zeta^2 F(1, \bar{R}).$$

We simplify our notation by writing $T(1, \bar{R}) \equiv T(\bar{R})$ and $F(1, \bar{R}) \equiv F(\bar{R})$.

Inserting $\zeta^2 T(\bar{R})$ and $\zeta^2 F(\bar{R})$ into Eq. (2) yields

$$R(d/dR)[\zeta^2(\bar{R})F(\bar{R})] + 2\zeta^2(\bar{R})F(\bar{R})$$
$$= (d/dR)[\zeta^2(\bar{R})T(\bar{R})], \qquad (3)$$

where we interpret ζ as a function of $\bar{R}$. We now transform the derivatives in Eq. (3) as follows: Since $d/dR = (d\bar{R}/dR)(d/d\bar{R})$ and

$$\frac{dR}{d\bar{R}} = \frac{d}{d\bar{R}} \cdot \frac{\bar{R}}{\zeta(\bar{R})} = \frac{1}{\zeta(\bar{R})} - \frac{\bar{R}}{\zeta^2(\bar{R})}\frac{d\zeta(\bar{R})}{d\bar{R}}$$
$$= \frac{1}{\zeta(\bar{R})}\left(1 - \bar{R}\frac{d}{d\bar{R}}\ln\zeta(\bar{R})\right),$$

we have $\quad \dfrac{d}{dR} \equiv \dfrac{\zeta(\bar{R})}{1 - \bar{R}(d/d\bar{R})\ln\zeta(\bar{R})}\dfrac{d}{d\bar{R}}. \qquad (4)$

Using this result, Eq. (3) becomes

$$\bar{R}(d/d\bar{R})[\zeta^2(\bar{R})F(\bar{R})]$$
$$+ 2[1 - \bar{R}(d/d\bar{R})\ln\zeta(\bar{R})]\zeta^2(\bar{R})F(\bar{R})$$
$$= \zeta(\bar{R})(d/d\bar{R})[\zeta^2(\bar{R})T(\bar{R})]. \qquad (5)$$

After some manipulation this reduces to

$$2T(\bar{R})d\zeta(\bar{R})/d\bar{R} + \zeta(\bar{R})dT(\bar{R})/d\bar{R}$$
$$- \bar{R}dF(\bar{R})/d\bar{R} - 2F(\bar{R}) = 0 \qquad (6)$$

or

$$d\zeta(\bar{R})/d\bar{R} + \{d[\ln T^{1/2}(\bar{R})]/d\bar{R}\}\zeta(\bar{R})$$
$$= [2F(\bar{R}) + \bar{R}\,dF(\bar{R})/d\bar{R}]/2T(\bar{R}). \qquad (7)$$

This equation will be recognized as a first-order, linear, inhomogeneous differential equation, the solution of which is immediate. In terms of an arbitrary integration limit $\bar{R}_0$, we have

$$\zeta(\bar{R}) = \left(\frac{T(\bar{R}_0)}{T(\bar{R})}\right)^{1/2}\left(\zeta(\bar{R}_0) - \frac{1}{2T^{1/2}(\bar{R})}\right.$$
$$\left. \times \int_{\bar{R}}^{\bar{R}_0}\frac{2F(R) + RdF(R)/dR}{T^{1/2}(R)}dR\right), \qquad (8)$$

which is the electrostatic-virial expression for the scale factor. Note that, unlike the variational expression for ζ, which contains two-electron integrals, Eq. (8) involves only the one-electron force and kinetic-energy integrals. Two-electron effects enter Eq. (8) only through $\zeta(\bar{R}_0)$. The relation of the EV scale factor to the variational scale factor is discussed next.

IV. THE VARIATIONAL SCALE FACTOR

It will now be shown that certain variational densities satisfy an electrostatic-virial theorem. This follows from a theorem due to Hurley,[3] which states that for any completely optimized variational wave function both the electrostatic and virial theorems are satisfied. That is, not

only are Eqs. (1) satisfied in the exact case but also in the case where *every* parameter in the wave function is variationally chosen. In order to make this completely clear, we will give a brief version of the proof.

Consider an electronic wave function for an N-electron diatomic molecule. Let the only R-dependence in this wave function be via variational parameters $\mu_i(R)$; then

$$\Psi = \Psi[\vec{r}_1 \ldots \vec{r}_N; \mu_1(R) \ldots \mu_k(R)].$$

Since the electronic Hamiltonian

$$\hat{H} \equiv -\tfrac{1}{2} \sum_i \nabla_i^2 + \sum_i V_i + \sum_{i<j} V_{ij}$$

is also R dependent, the R dependence of $E = \langle \Psi \mid \hat{H} \mid \Psi \rangle$ derives from two different sources. We therefore can write dE/dR as

$$\frac{dE}{dR} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial R} \right| \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial R} \left| \hat{H} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{H} \right| \frac{\partial \Psi}{\partial R} \right\rangle. \quad (9)$$

But by hypothesis

$$\frac{\partial \Psi}{\partial R} = \sum_i^k \frac{\partial \mu_i}{\partial R} \frac{\partial \Psi}{\partial \mu_i}$$

so that

$$\frac{dE}{dR} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial R} \right| \Psi \right\rangle + \sum_i^k \frac{d\mu_i}{dR} \frac{\partial}{\partial \mu_i} \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle. \quad (10)$$

But the variational condition is $(\partial/\partial\mu_i) \langle \Psi | \hat{H} | \Psi \rangle \equiv 0$ for all μ_i. Thus

$$\frac{dE}{dR} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial R} \right| \Psi \right\rangle = \int \frac{\partial V_1}{\partial R} \rho_1(\vec{r}, R) d^3 r \equiv -F, \quad (11)$$

where $\partial \hat{H}/\partial R$ and $\partial V_1/\partial R$ are calculated holding all variational parameters fixed. Thus, provided $\rho_1(\vec{r}, R)$ is completely optimized, the electrostatic theorem is satisfied.

We now show, following Coulson and Bell,[4] that a variationally optimized ζ is sufficient to ensure satisfaction of the virial theorem. Defining

$$V(\zeta, R) \equiv \left\langle \Psi \left| \sum_i^N V_i + \sum_{i<j} V_{ij} \right| \Psi \right\rangle,$$

where Ψ is the scaled wave function, we have

$$E(\zeta, R) = \zeta^2 T(\overline{R}) + \zeta V(\overline{R})$$

by the usual dimensional arguments. Thus $[\partial E(\zeta, R)/\partial\zeta]_R = 0$ implies that

$$2\zeta T(\overline{R}) + V(\overline{R}) + \zeta \overline{R} \frac{dT(\overline{R})}{d\overline{R}} + \overline{R} \frac{dV(\overline{R})}{d\overline{R}} = 0. \quad (12)$$

Multiplying Eq. (11) by ζ and using

$$dT(\overline{R})/d\overline{R} = \zeta^{-1}[\partial T(\overline{R})/\partial R]_\zeta$$

and

$$dV(\overline{R})/d\overline{R} = \zeta^{-1}[\partial V(\overline{R})/\partial R]_\zeta,$$

we have

$$2T(\zeta, R) + V(\zeta, R)$$
$$+ R[\partial T(\zeta, R)/\partial R]_\zeta + R[\partial V(\zeta, R)/\partial R]_\zeta = 0. \quad (13)$$

But since

$$V(\zeta, R) = E(\zeta, R) - T(\zeta, R),$$

Eq. (13) takes the form

$$\overline{R}[\partial E(\zeta, R)/\partial \overline{R}]_\zeta = R[\partial E(\zeta, R)/\partial R]_\zeta$$

$$= -E(\zeta, R) - T(\zeta, R). \quad (14)$$

However,

$$dE(\zeta, R)/dR \equiv [\partial E(\zeta, R)/\partial R]_\zeta$$

because $[\partial E(\zeta, R)/\partial\zeta]_R = 0$

for all R; therefore

$$R\,dE(\zeta, R)/dR + E(\zeta, R) = -T(\zeta, R) \quad (15)$$

which is the usual form of the virial theorem. Thus both the electrostatic and virial theorems [Eqs. (11) and (15)] are satisfied for a wave function in which all parameters, including a scale factor, are variationally determined (Hurley's theorem).

The EV theorem for completely optimized densities now follows upon differentiating Eq. (15) with respect to R using Eq. (11), viz.

$$R\,dF(\zeta, R)/dR + 2F(\zeta, R) = -dT(\zeta, R)/dR. \quad (16)$$

The differential equation for the scale factor, Eq. (3), follows upon showing that $F(\zeta, R) = \zeta^2 F(1, \overline{R})$. But this can be shown using Eq. (11) and the fact that the one-body Coulomb potential V_1 is homogeneous of degree -1 in r and R. Thus

$$-F(\zeta, R) \equiv dE(\zeta, R)/dR$$

$$= \int \left(\frac{\partial V_1(\vec{r}, R)}{\partial R} \right)_\zeta \zeta^3 \rho_1(\zeta\vec{r}, \zeta R) d^3 r$$

$$= \zeta^2 \int \left(\frac{\partial V_1(\zeta\vec{r}, \zeta R)}{\partial(\zeta R)} \right)_\zeta \rho_1(\zeta\vec{r}, \zeta R) d^3(\zeta r)$$

$$\equiv -\zeta^2 F(\overline{R}). \quad (17)$$

A comparison can now be made to the conventional variational ζ formula.[4] Solving Eq. (12) for ζ, we obtain the well-known expression,

$$\zeta(R) = \frac{V(\overline{R}) + \overline{R}\,dV(\overline{R})/d\overline{R}}{2T(\overline{R}) + \overline{R}\,dT(\overline{R})/d\overline{R}}, \quad (18)$$

which does not depend on the variational optimization of other parameters. This is in contrast to the EV expression

$$\zeta(\overline{R}) = \left(\frac{T(\overline{R}_0)}{T(\overline{R})}\right)^{1/2} \left(\zeta(\overline{R}_0) - \frac{1}{2T^{1/2}(\overline{R}_0)}\right.$$

$$\left. \times \int_{\overline{R}}^{\overline{R}_0} \frac{2F(R) + R\,dF(R)/dR}{T^{1/2}(R)} dR\right) \quad , \quad (8)$$

which requires that $\partial E/\partial\mu_i \equiv 0$ for all i. On the other hand, Eq. (18) contains (via V) both the one- and two-body densities while Eq. (8) has the advantage of involving only the one-body density.

V. APPLICATIONS OF THE ELECTROSTATIC-VIRIAL ζ FORMULA

A. General

The equivalence of the EV and standard variational scale factors, discussed above, will seldom be met in practice; as a rule, one is not presented with a density which is completely optimized. Particular difficulties are presented by relatively small (limited basis) calculations which fail to optimize the so-called "floating" parameter. This parameter, first introduced by Gurney and Magee,[5] allows the base functions to be displaced from the nuclei. Hurley[3] and more recently Shull and Ebbing,[6] have variationally determined a scale and floating parameters for some simple molecular-orbital (MO) and valence-bond (VB) wave functions for $H_2{}^+$ and H_2. These functions constitute examples of complete optimization. The floating parameter $X(R)$ is largest in the neighborhood of equilibrium, attaining values of 0.1 a.u. for $H_2{}^+$ (MO), ≈ 0.05 a.u. for H_2 (MO), and ≈ 0.06 a.u. for H_2 (VB). Although $X(R)$ can be as large as 5–10% of the internuclear separation, the corresponding energies and scale factors differ from the unfloated variational values by less than 1%. On the other hand, several calculations[3,7] have shown that the "floated" and "unfloated" Hellman-Feynman forces differ considerably. In general, therefore, we do not expect the EV theorem to be quantitatively applicable to simple unfloated densities. Conversely, the EV theorem should be exactly satisfied if *all* parameters, including X are variationally determined. This was computationally verified in the case of the variationally floated H_2 MO of Shull and Ebbing. Using their values of X, the EV ζ formula, Eq. (8), was used to reproduce their variational scale factor. The following calculations, using standard unfloated densities, will serve to amplify the above discussion and at the same time provide examples of the use of the EV ζ formula.

B. The $H_2{}^+$ Molecule

The EV scale-factor curve for the unfloated is $1s_{\sigma_g}$ wave function for $H_2{}^+$ is displayed in Fig. 1 The variational integration limit[8]

$$\zeta(\overline{R}_0) = \zeta(\infty) = 1$$

has been used. Note that the EV ζ curve, although manifesting qualitatively correct behavior, is in poor agreement with the variational values for
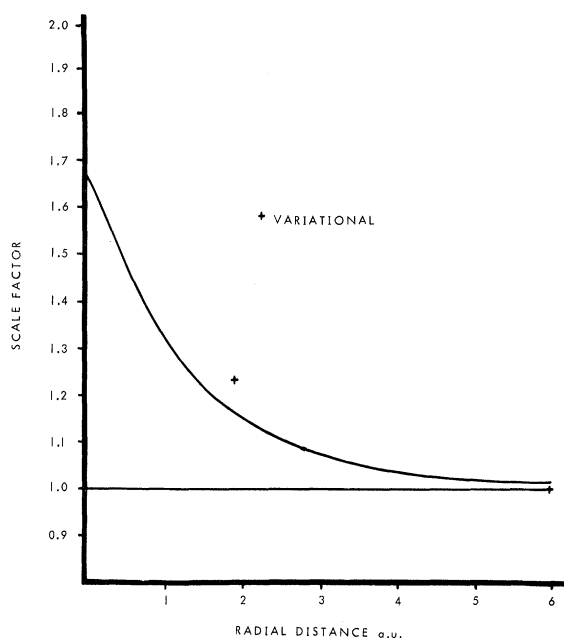

FIG. 1. ζ curve for $H_2{}^+$ $1s_{\sigma_g}$ $[\zeta(\infty) = 1]$. Comparison variational ζ's are indicated by crosses.

small R. The total energy

$$U(R) = E(R) + Z_A Z_B/R$$

resulting from the corresponding scaled density exhibits no minimum. Thus the neglect of floating in applying the EV ζ formula to this case is a severe approximation. This is consistent with Hurley's electrostatic calculation of the $H_2{}^+$ energy using the unfloated $1s_{\sigma_g}$ function, which also predicted instability.[3]

C. The H_2 Molecule

Several EV scale-factor curves were computed for the H_2 $1s_{\sigma_g}$ wave function. Curve III in Fig. 2 has $\zeta(\infty)$ adjusted to the variational value 0.843 75.[8] As in $H_2{}^+$, the EV ζ curve increases too slowly with decreasing R, indicating a significant effect due to neglect of floating. However, the agreement with the variational result is better than in $H_2{}^+$, in accord with the relatively smaller values of the floating parameter given above. Curve I of Fig. 2 is for $\zeta(\infty) = 1$, which is the "experimental" scale factor corresponding to dissociation into two neutral hydrogen atoms. Curve II of Fig. 2 is for ζ adjusted to the variational value of 1.2 at the equilibrium distance 1.4 a.u. The changes in integration limits are seen to cause very nearly parallel displacements of the curves, resulting in improved values of ζ for small R.

The total energy curves for $\zeta(\infty) = 0.843\,75$ and for $\zeta(\infty) = 1.0$ are displayed in Fig. 3, along with the highly accurate Kolos-Roothaan[9] energy curve and the MO variational values for $R = 1.4$ and $R \to \infty$. Here, in contrast to $H_2{}^+$, the qualitative behavior of the energies is rather good, reflecting a smaller error due to neglect of floating.

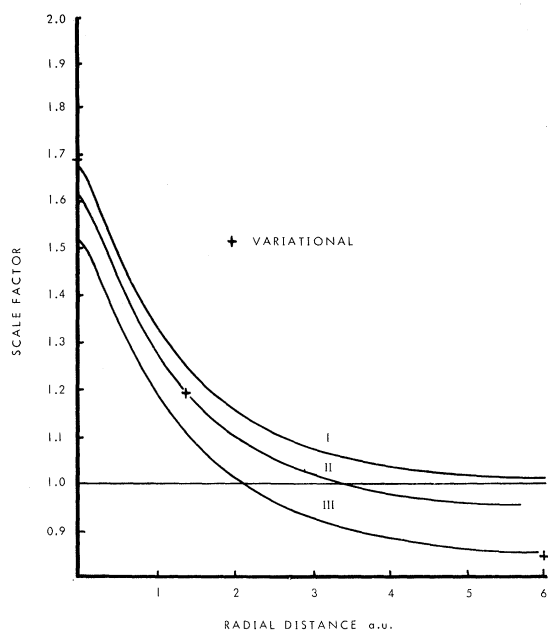Qualitatively similar results were obtained for the EV scaled valence-bond density for H_2.

FIG. 2. ζ curves for H_2 $1s_{\sigma g}$: I, $\zeta(\infty) = 1.0$; II, $\zeta(1.4)$ $= 1.2$; and III, $\zeta(\infty) = 0.843\,75$. Comparison variational ζ's are indicated by crosses.

D. The He₂ Molecule

For He₂, a single EV scale factor is computed for a density having two electrons each in $1s_{\sigma g}$ and $1s_{\sigma u}$ orbitals. In this case we write the $1s$ function as, e.g.,

$$1s_A = (\xi^{3/2}/\sqrt{\pi}) \exp(-\xi r_A)$$

where $\xi(R) = \zeta(R)\xi(\infty)$ and $\xi(\infty) = 1.6875$, the variational separated-atom exponent for He.[10] The EV $\xi(R)$

FIG. 4. Scale-factor curve and He₂: $\xi(\infty) = 1.6875$ [$\zeta(\infty) = 1$].

curve is given in Fig. 4. There exists no corresponding variational calculation for comparison. In Fig. 5 we present our EV energy along with that of Phillipson's extensive configuration-interaction calculation.[11] In this case we observe essentially quantitative agreement for 1.5 a. u. $<R<\infty$. The goodness of the energy here is not alone sufficient to sustain a conclusion as to the importance of floating in this limited basis He₂
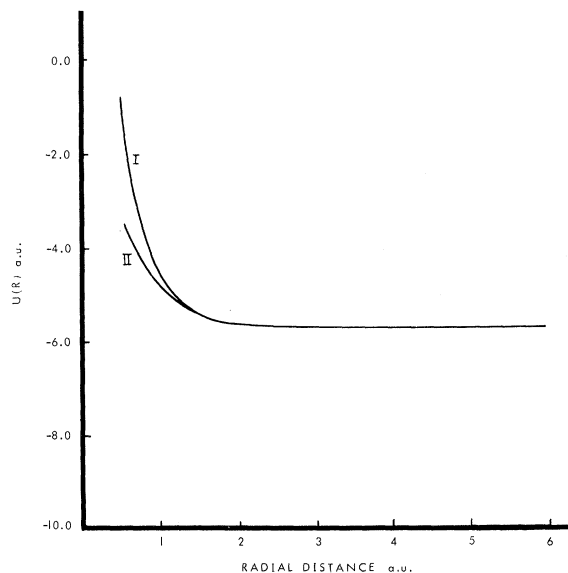

FIG. 3. Energy comparison for H_2 $1s_{\sigma g}$: I, $\zeta(\infty)$ $= 0.843\,75$; II, $\zeta(\infty) = 1.0$; and III, best theoretical curve (Ref. 9).

FIG. 5. Energy comparison for He₂: I, our EV calculation; and II, best variational curve (Ref. 11).

density. Nevertheless, it does encourage one to suspect that neglect of floating may not cause serious errors in similar inert interactions described in limited bases. If this suspicion is borne out, the EV ζ formula will enable one to obtain reliable interaction-energy curves with relative ease.

VI. IDEMPOTENT DENSITY-MATRIX CONTINUATION EQUATIONS

In previous sections we have been concerned with scaled densities without unknown linear parameters. We will now consider the problem of a fixed basis and concern ourselves with the variation of the density matrix P with respect to a parameter λ. The particular application of interest here is when $\lambda = R$ and the constraint is the EV theorem.

Consider the pure-state (idempotent) density matrix $P(\lambda)$ in an orthogonal basis. We require $P(\lambda + \Delta\lambda)$ to be idempotent and to satisfy a certain set of constraints $\mathrm{Tr}PO_i = O_i$ to first-order in $\Delta\lambda$. We first expand all quantities in powers of $\Delta\lambda$:

$$P(\lambda + \Delta\lambda) = P(\lambda) + P'(\lambda)\Delta\lambda + \cdots, \qquad (19a)$$

$$P^2(\lambda + \Delta\lambda) = P^2(\lambda)$$
$$+ [P(\lambda)P'(\lambda) + P'(\lambda)P(\lambda)]\Delta\lambda + \cdots, \quad (19b)$$

$$\mathrm{Tr}P(\lambda + \Delta\lambda)O_i(\lambda + \Delta\lambda) = \mathrm{Tr}P(\lambda)O_i(\lambda)$$
$$+ [\mathrm{Tr}P'(\lambda)O_i(\lambda) + \mathrm{Tr}P(\lambda)O_i'(\lambda)]\Delta\lambda + \cdots,$$

$$O_i(\lambda + \Delta\lambda) = O_i(\lambda) + O_i'(\lambda)\Delta\lambda + \cdots. \qquad (19c)$$

Now, by hypothesis, $P^2(\lambda) = P(\lambda)$. Thus the first-order idempotency condition is

$$P(\lambda)P'(\lambda) + P'(\lambda)P(\lambda) - P'(\lambda) = 0, \qquad (20)$$

and P' is subject to the first-order constraining conditions

$$\mathrm{Tr}[P'(\lambda)O_i(\lambda) + P(\lambda)O_i'(\lambda)] = O_i'(\lambda). \qquad (21)$$

Idempotency of $P(\lambda + \Delta\lambda)$ implies

$$P(\lambda + \Delta\lambda) = C(\lambda + \Delta\lambda)C^\dagger(\lambda + \Delta\lambda)$$
$$= [C(\lambda) + C'(\lambda)\Delta\lambda + \cdots][C^\dagger(\lambda) + C'^\dagger(\lambda)\Delta\lambda + \cdots] \quad (22)$$

so that to first order we have

$$P(\lambda + \Delta\lambda) = C(\lambda)C^\dagger(\lambda)$$
$$+ [C(\lambda)C'^\dagger(\lambda) + C'(\lambda)C^\dagger(\lambda)]\Delta\lambda. \qquad (23)$$

Comparing Eqs. (19) and (23), we see that

$$P'(\lambda) = C(\lambda)C'^\dagger(\lambda) + C'(\lambda)C^\dagger(\lambda). \qquad (24)$$

Inserting this expression into Eqs. (21) yields a system of linear equations for the elements of $C'(\lambda)$, since $C(\lambda)$ and $P(\lambda)$ are assumed known. It is now obvious that the number of constraining conditions [Eqs. (21)] is equal to the number of elements of $C'(\lambda)$.

Consider the case where $\lambda = R$. Since the EV theorem

$$RdF/dR + 2F = dT/dR$$

takes the matrix form

$$\mathrm{Tr}[P'(RF - T) + P(RF' + 2F - T')] = 0, \qquad (25)$$

It can be immediately incorporated as a constraint [compare Eq. (21)] in the continuation of the density matrix P from R to $R + \Delta R$.

VII. SUMMARY AND CONCLUSION

An electrostatic-virial (EV) theorem, which is an exact integrodifferential condition on the one-body density matrix alone has been derived. This theorem results very simply from the combined use of the electrostatic and virial theorems, which separately involve both the one- and two-body densities.

In the present work, the particular application of the EV theorem to a scaled density is worked out in detail, resulting in the scale-factor formula of Eq. (8). It was shown that under certain conditions this formula yields the conventional variational scale factor. The several calculations performed re-emphasize the importance of complete variational parameter optimization in the use of the electrostatic theorem.

Finally, a formalism was developed in which the EV theorem serves as a constraint on the derivative of an idempotent density matrix with respect to internuclear distance.

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