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# Energy–Density Relations in Momentum Space

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The integrated Hellmann–Feynman theorem is used to derive a rigorous relation between the energy and the electron density in momentum space. Choosing the electron mass as a differential parameter, we obtain a formula corresponding to the Wilson–Frost formula in coordinate space. Analysing the mass-dependence of momentum density, we then show that the present formula is equivalent to one of the previous results deduced from the virial theorem. Use of the integral Hellmann–Feynman theorem is also discussed. Several illustrative examples are given for the calculation of energy from momentum density.

**Key words:** Momentum electron density – Hellmann–Feynman theorem.

## 1. Introduction

In 1962, Wilson [1] showed that the electronic energy of a molecular system can be calculated from the electron density $\rho(\boldsymbol{r})$ by the use of the Hellmann–Feynman (H–F) theorem [2–5] with respect to nuclear charge $Z$ (Wilson charging process). Frost [6] then introduced the average electron density function and simplified the Wilson's formalism. Epstein et al. [7] showed that the Wilson charging process (see also [8]) is an application of the integrated H–F theorem, and gave detailed analysis in comparison with the integral H–F theorem [9]. Wilson's idea has been also generalized to the case where nuclear motion is taken into account [10].

On the other hand, we have recently proposed a method of momentum density [11] which permits to clarify the origin of nuclear rearrangements (such as molecular geometries and chemical reactions) in terms of the concept in momentum ($p$-) space instead of the usual one in coordinate ($r$-) space. The approach

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has been motivated by the fact that in quantum mechanics the position $\boldsymbol{r}$ and the momentum $\boldsymbol{p}$ of a particle are variables which can equally describe states of systems under the commutation condition $[\boldsymbol{r}, \boldsymbol{p}] = i$ [12]. Applying the *virial theorem* to a uniform scaling process [13], we have derived three rigorous formulas for the total energy of a system using the momentum electron density $\rho(\boldsymbol{p})$ as a basic physical quantity. It has been then suggested that the contraction and expansion of $\rho(\boldsymbol{p})$ is an important concept which characterizes the nature of nuclear rearrangements in $p$-space. The method has been applied to the $\sigma$ and $\pi$ states of $H_2^+$ system and the processes of the attractive and repulsive interactions have been analysed in detail based on the reorganization of $\rho(\boldsymbol{p})$ [14].

The purpose of this paper is to show that a rigorous relation between the energy $E$ and the momentum density $\rho(\boldsymbol{p})$ can *also* be deduced from the *H–F theorem.* By the application of the H–F theorem with respect to the electron mass $m$ [15, 16], $dE/dm$ is given as a function of kinetic energy $T$. Since $T$ is simply related to $\rho(\boldsymbol{p})$ in $p$-space $[T = \int d\boldsymbol{p}(p^2/2)\rho(\boldsymbol{p})]$, the integrated H–F theorem then enables us to determine $E$ from the knowledge of $\rho(\boldsymbol{p})$. The resultant equation in $p$-space corresponds to the Wilson's equation in $r$-space. If the nuclear mass $M$, instead of the electron mass $m$, is taken as a parameter, the present result is also applicable to the study of nuclear isotope effect. Moreover, analysis of the $m$-dependence shows that $m$ enters into wavefunctions just as a scale parameter. Then, the present formula derived from the integrated H–F theorem is proved to be an alternative form of one of the previous results derived from the virial theorem. Application of the integral H–F theorem is also discussed. This theoretical consideration is developed in the next section. Simple applications of the present results are given in Sect. 3.

## 2. Energy–Momentum Density Relations

### 2.1. Integrated Hellmann–Feynman Theorem

We consider a molecular system with $N$ electrons whose electronic Hamiltonian, wavefunction, and energy are $H$, $\Psi$, and $E$, respectively. Then the energy difference between two states $\Psi(\lambda_1)$ and $\Psi(\lambda_2)$ specified by a parameter $\lambda$ embedded in $H$, $\Psi$, and $E$ is given by the integrated H–F theorem [7] as

$$\begin{aligned}\Delta E &\equiv E(\lambda_2) - E(\lambda_1)\\ &= \int_{\lambda_1}^{\lambda_2} d\lambda \langle \Psi(\lambda) | [\partial H(\lambda)/\partial\lambda] | \Psi(\lambda) \rangle,\end{aligned} \tag{1}$$

where $\Psi(\lambda) = \Psi(\{\boldsymbol{r}_i\}; \lambda)$ is assumed to be normalized and $\{\boldsymbol{r}_i\}$ $(i = 1, \dots, N)$ denote position vectors of electrons. Atomic units are used throughout this paper.

If the electron mass $m$ is taken as $\lambda$, Eq. (1) becomes

$$\Delta E = -\int_{m_1}^{m_2} dm\, m^{-2}\left\langle \Psi(m) \middle| \left[(-1/2)\sum_i \partial^2\big/\partial r_i^2\right] \middle| \Psi(m)\right\rangle$$

$$= -\int_{m_1}^{m_2} dm\, m^{-2} \int d\boldsymbol{r}[(-1/2)(\partial^2/\partial \boldsymbol{r}^2)\rho(\boldsymbol{r}', \boldsymbol{r}; m)]_{r'=r}, \tag{2}$$

since only the kinetic energy operator $T_{\text{op}} = -(2m)^{-1}\sum_i \partial^2/\partial r_i^2$ depends on $m$ in the Hamiltonian. Here, $\rho(\boldsymbol{r}', \boldsymbol{r}; m)$ $[\equiv N \int d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N \Psi^*(\boldsymbol{r}', \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N; m)$ $\Psi(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N; m)]$ is the first-order density matrix in $r$-space. If we use the $p$-representation, Eq. (2) is rewritten as

$$\Delta E = -\int_{m_1}^{m_2} dm\, m^{-2} \int d\boldsymbol{p}(p^2/2)\rho(\boldsymbol{p}; m)$$

$$= -\int d\boldsymbol{p}\, (p^2/2)\hat{\rho}(\boldsymbol{p}), \tag{3a}$$

$$\hat{\rho}(\boldsymbol{p}) \equiv \int_{m_1}^{m_2} dm\, m^{-2}\rho(\boldsymbol{p}; m), \tag{3b}$$

where $\boldsymbol{p}$ stands for the momentum vector of an electron and $p = |\boldsymbol{p}|$. $\rho(\boldsymbol{p}; m)$ $[\equiv N \int d\boldsymbol{p}_2 \cdots d\boldsymbol{p}_N |\Psi(\boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N; m)|^2]$ means momentum electron density, i.e. the diagonal element of the first-order density matrix in $p$-space. Since the kinetic energy operator $(p^2/2)$ appearing in Eq. (3a) is angular-independent, Eq. (3) is further simplified by the use of the radial momentum density $I(p)$ $[\equiv \int d\theta_p\, d\phi_p\, p^2 \sin\theta_p\, \rho(\boldsymbol{p})]$ instead of the three-dimensional $\rho(\boldsymbol{p})$. That is

$$\Delta E = -\int dp\, (p^2/2)\hat{I}(p), \tag{4a}$$

$$\hat{I}(p) \equiv \int_{m_1}^{m_2} dm\, m^{-2} I(p; m). \tag{4b}$$

Eqs. (3) and (4) are the desired results. In the above derivation, two properties of the kinetic energy operator are fully utilized; (*i*) it is a multiplicative operator in $p$-space, (*ii*) it is the only $m$-dependent expression in the Hamiltonian.

Eqs. (3) and (4) show that we can rigorously relate the energy change $\Delta E$ with the momentum densities $\rho(\boldsymbol{p})$ and $I(p)$ by considering the fictitious process where electron mass varies from $m_1$ to $m_2$. Specifically, $m = 1$ represents the normal electron and the integration from an appropriate $m_1$ to $m_2 = 1$ gives the energy of a system by $E = \Delta E + E(m_1)$. Furthermore, it is convenient to choose $m_1 = 0$, since $E \propto m$ and hence $E(0) = 0$ (see also [15]). We can thus calculate the energy itself from the momentum density by carrying out the integration of Eqs. (3b) and (4b) from $m = 0$ to 1.

The present equation in $p$-space seems to correspond to Wilson's equation [1] in $r$-space. The two methods may be complementary in the sense that they connect energy with densities in the two different spaces. In the $r$-space, the energy–density formula is derived from the relation between the nuclear–electron attraction potential $(-Z_A/|\boldsymbol{r}-\boldsymbol{R}_A|)$ and the coordinate density $\rho(\boldsymbol{r})$, while in the $p$-space, it is derived from the relation between the kinetic energy $(p^2/2)$ and the momentum density $\rho(\boldsymbol{p})$. The new density function $\hat{\rho}(\boldsymbol{p})$ corresponds to the average electron density $p(\boldsymbol{r}) = \int_0^1 dZ\, \rho(r; Z)$ introduced by Frost [6]. When the two methods are applied to the molecular electron density obtained from LCAO wavefunctions, Wilson's formula requires the evaluation of integrals up to three-center type, whereas the present formula requires up to two-center type. This is a merit of the present equation.

The present method can be also applied to the nuclear problem (see also [16]). For example, equations of the same form as Eqs. (3) and (4) are obtained by substituting $H$, $\Psi$, and $E$ in the above formulation by $(T_{\mathrm{op}}^{\mathrm{nuc}} + E)$, $\Phi$, and $W$ for the nuclear motion in the Born–Oppenheimer approximation, and by taking the nuclear mass $M$ as a parameter. In this case, $\Delta W\ [\equiv W(M_2) - W(M_1)]$ implies the energy difference due to isotope effect. Therefore, the present method may provide an interesting way to investigate the relation between the isotopic energy change and the nuclear momentum density distribution.

## *2.2. Approximate Momentum Density and Virial Theorem*

Though it is assumed in the preceding formalism that $\rho(\boldsymbol{p})$ is known exactly, Eqs. (3) and (4) can be shown to be also valid for a kind of approximate momentum densities.

Following Hurley, we consider an energy expression $\varepsilon(\mu, m) = \langle\Psi(m)|H(\mu)|\Psi(m)\rangle$, distinguishing the parameters $m$ in $\Psi$ and $H$. Then the H–F and integrated H–F theorems hold if $\partial\varepsilon(\mu, m)/\partial m = 0$ [5, 7, 17]. The wavefunction which satisfies this condition is called floating function and we investigate it here. Analysis of the explicit $m$-dependence of the wavefunction shows that $m$ appears as

$$\begin{aligned}\Psi(m) &= m^{3N/2}\psi_r(\{m\boldsymbol{r}_i\}; m\boldsymbol{R}) \quad \text{(in } r\text{-space)}\\ &= m^{-3N/2}\psi_p(\{m^{-1}\boldsymbol{p}_i\}; m\boldsymbol{R}) \quad \text{(in } p\text{-space)}\end{aligned} \tag{5}$$

where $\boldsymbol{R} \equiv \{\boldsymbol{R}_A\}$ denotes the space coordinates of nuclei and $N$ is the number of electrons. It is clear then that $m$ works as a scale factor in the wavefunction. The condition $\partial\varepsilon(\mu, m)/\partial m = 0$ is satisfied by scaled wavefunctions in which optimum scale factors are variationally determined. Consequently, scaled wavefunctions satisfy the H–F theorem with respect to $m$ and hence Eqs. (3) and (4) are valid for the resultant momentum densities. It is interesting that the scaled wavefunction is a floating wavefunction with respect to $m$.

Keeping in mind that the scaled wavefunction satisfies the virial theorem [18], we next investigate a relationship between Eq. (3) and the Eqs. [11] derived from the virial theorem previously.

From Eq. (5), we obtain a scaling relation for the momentum electron density,

$$\rho(\boldsymbol{p}; \boldsymbol{R}, m) = m^{-3}\rho(m^{-1}\boldsymbol{p}; m\boldsymbol{R}, 1), \tag{6}$$

where the nuclear conformation $\boldsymbol{R}$ is explicitly written as another parameter. Using this relation with $m_1 = 0$ and $m_2 = 1$, we can rewrite Eq. (3a) as

$$E = -\int_0^1 dm \int d\boldsymbol{p}(p^2/2)\rho(\boldsymbol{p}; m\boldsymbol{R}, 1). \tag{7a}$$

If we consider a uniform scaling process of an arbitrary conformation $\boldsymbol{R}_0$, $\boldsymbol{R} = s\boldsymbol{R}_0$, Eq. (7a) is further reduced to

$$E = -(1/s) \int_0^s ds' \int d\boldsymbol{p}\, (p^2/2)\rho(\boldsymbol{p}; s', 1), \tag{7b}$$

where the scale factor $s$ varies from 0 (united atom limit) to $\infty$ (separated atoms limit). Eq. (7b) is identical with one of the three equations derived previously [11]. Namely, the integrated H–F theorem with respect to $m$ and the virial theorem for a uniform scaling process are equivalent. This is an expected result from the equality of the floating and scaled wavefunctions in the present case. In the special case of atoms, Eq. (7) is simplified to $E = -\int d\boldsymbol{p}\, (p^2/2)\rho(\boldsymbol{p})$, which is nothing but the atomic virial theorem $E = -T$. However, we note that $\rho(\boldsymbol{p})$ and $\hat{\rho}(\boldsymbol{p})$ (or $I(p)$ and $\hat{I}(p)$) are different even for atoms.

### 2.3. *Integral Hellmann–Feynman Theorem*

We here briefly discuss an application of the integral H–F theorem [5, 7, 9] to the $E$–$\rho(\boldsymbol{p})$ problem. From the integral H–F theorem,

$$\Delta E = \langle\Psi(\lambda_1)|[H(\lambda_2) - H(\lambda_1)]|\Psi(\lambda_2)\rangle/\langle\Psi(\lambda_1)|\Psi(\lambda_2)\rangle, \tag{8}$$

we obtain

$$\Delta E = -\int d\boldsymbol{p}\, (p^2/2)\hat{\rho}_{12}(\boldsymbol{p}), \tag{9a}$$

$$\hat{\rho}_{12}(\boldsymbol{p}) \equiv (m_1^{-1} - m_2^{-1})\rho_{12}(\boldsymbol{p})/S_{12}, \tag{9b}$$

by setting $\lambda = m$ and using the $p$-representation. $\rho_{12}(\boldsymbol{p})$ [$\equiv N \int d\boldsymbol{p}_2 \cdots d\boldsymbol{p}_N \cdot \Psi^*(\boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N; m_1)\Psi(\boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N; m_2)$] is the transition density and $S_{12}$ [$\equiv\langle\Psi(m_1)|\Psi(m_2)\rangle$] the transition overlap between the states $\Psi(m_1)$ and $\Psi(m_2)$. Eq. (9) enables us to obtain $\Delta E$ from the knowledge of the transition density $\rho_{12}(\boldsymbol{p})$. Application to the nuclear isotope effect is straightforward. Simplification by the use of the radial transition density $I_{12}(p)$ [$\equiv\int d\theta_p\, d\phi_p\, p^2 \sin\theta_p\, \rho_{12}(\boldsymbol{p})$] is also possible.

When compared with the result of the integrated H–F theorem (Eq. (3)), Eq. (9) is more simple in that the latter does not include integration about $m$. However, the required quantity is the transition density $\rho_{12}(\boldsymbol{p})$ and not the density $\rho(\boldsymbol{p})$ itself. The result of the integral H–F theorem therefore deviates from our purpose to connect $E$ and $\rho(\boldsymbol{p})$ in a quantitative manner. In this sense, Eq. (9) seems to be a new formula which does not reduce to the results of the virial and integrated H–F theorems.

For approximate transition densities, Eq. (9) is valid only when parent wavefunctions are superfloating [5, 7, 19]. The condition of superfloating is more restrictive than that of floating, and the scaled wavefunction is not superfloating with respect to the parameter $m$. It may be, however, possible to construct a superfloating wavefunction by the linear variation using $\Psi(m_1)$ and $\Psi(m_2)$ as a basis set [5, 7, 19].

## 3. Illustrative Examples

In this section, the energy–momentum density relations are exemplified for several cases. First, the electronic energy of atoms and molecules is discussed based on both the exact and approximate momentum densities. Secondly, the vibrational energy of diatomic molecules is examined as an example of nuclear isotope effect. All the momentum densities are derived from the Dirac–Fourier transform [12] of the corresponding $r$-space wavefunctions.

### *3.1. Electronic Energy*

### 3.1.1. Atomic Case

Since Eq. (7) for atoms reduces to the ordinary virial theorem, we here show applications of Eq. (4). Let us consider a ground-state hydrogen-like atom with nuclear charge $Z$. We first deal with the exact momentum density. The $p$-space wavefunction corresponding to $1s(\mathbf{r}; m) = (m^3 Z^3/\pi)^{1/2} \exp(-mZr)$ is given by [20]

$$1s(\mathbf{p}; m) = (2^{3/2}/\pi)(mZ)^{5/2}\{p^2 + (mZ)^2\}^{-2}, \tag{10a}$$

and hence the radial momentum density by

$$I(p; m) = (2^5/\pi)(mZ)^5 p^2\{p^2 + (mZ)^2\}^{-4}. \tag{10b}$$

Then Eq. (4b) yields

$$\begin{aligned}\hat{I}(p) = (2^3/\pi)Zp^2[&\{p^2/3 + (m_1Z)^2\}\{p^2 + (m_1Z)^2\}^{-3} \\ &-\{p^2/3 + (m_2Z)^2\}\{p^2 + (m_2Z)^2\}^{-3}],\end{aligned} \tag{11a}$$

and Eq. (4a) results in

$$\Delta E = -(Z^2/2)(m_2 - m_1). \tag{11b}$$

By setting $m_1 = 0$ and $m_2 = 1$, we obtain the correct energy of the hydrogen-like atom, $-(Z^2/2)$. Since the exact wavefunction satisfies the integral H–F theorem, Eq. (9) also provides the correct energy. In this case, the radial transition densities $I_{12}(p)$ and $\hat{I}_{12}(p)$ are given by

$$I_{12}(p) = (2^5/\pi)(m_1m_2)^{5/2}Z^5p^2\{p^2 + (m_1Z)^2\}^{-2}\{p^2 + (m_2Z)^2\}^{-2}, \tag{12a}$$

$$\hat{I}_{12}(p) = (2^2/\pi)(m_2 - m_1)(m_1 + m_2)^3 Z^5 p^2\{p^2 + (m_1Z)^2\}^{-2}\{p^2 + (m_2Z)^2\}^{-2}. \tag{12b}$$

Next, we consider the case of approximate momentum density using a one-term Gaussian function $1s_{\mathrm{app}}(\boldsymbol{r}; m) = (2\alpha m^2/\pi)^{3/4} \exp(-\alpha m^2 r^2)$. The corresponding momentum wavefunction and radial density are found to be

$$1s_{\mathrm{app}}(\boldsymbol{p}; m) = (2\pi\alpha m^2)^{-3/4} \exp(-p^2/4\alpha m^2), \tag{13a}$$

$$I_{\mathrm{app}}(p; m) = (2/\pi\alpha^3)^{1/2} m^{-3} p^2 \exp(-p^2/2\alpha m^2), \tag{13b}$$

and then Eq. (4) results in

$$\begin{aligned}\hat{I}_{\mathrm{app}}(p) = (2/\pi\alpha)^{1/2}[&(m_2^{-2} + 2\alpha/p^2)\exp(-p^2/2\alpha m_2^2)\\ &-(m_1^{-2} + 2\alpha/p^2)\exp(-p^2/2\alpha m_1^2)],\end{aligned} \tag{14a}$$

$$\Delta E_{\mathrm{app}} = -(3/2)\alpha(m_2 - m_1). \tag{14b}$$

The result for $\Delta E_{\mathrm{app}}$ is different from that obtained by the calculation of energy expectations;

$$\Delta E'_{\mathrm{app}} = \{3\alpha/2 - 2(2\alpha/\pi)^{1/2} Z\}(m_2 - m_1). \tag{15}$$

However, if we adopt the variationally-determined optimum $\alpha$, $\alpha_{\mathrm{opt}} = 8Z^2/9\pi$, the two expressions coincide;

$$\Delta E_{\mathrm{app}} = \Delta E'_{\mathrm{app}} = -(4Z^2/3\pi)(m_2 - m_1). \tag{16}$$

This exemplifies that proper scaling is necessary in order that the present method holds for approximate momentum densities. On the other hand, this wavefunction is not superfloating even for $\alpha = \alpha_{\mathrm{opt}}$. Thus Eq. (9) results in

$$\begin{aligned}\hat{I}_{12,\mathrm{app}}(p) = {}&2^{-1}(\pi\alpha^3)^{-1/2}(m_2 - m_1)\\ &\times(m_1^2 + m_2^2)^{3/2}(m_1 m_2)^{-4} p^2 \exp(-p^2/4\alpha m_1^2 - p^2/4\alpha m_2^2),\end{aligned} \tag{17a}$$

$$\Delta E''_{\mathrm{app}} = -3\alpha m_1 m_2 (m_1^2 + m_2^2)^{-1}(m_2 - m_1), \tag{17b}$$

and gives incorrect answer for $m_1 = 0$ and $m_2 = 1$.

### 3.1.2. Molecular Case

We now consider an application of Eq. (7) to the ground $1s\sigma_g$ state of $H_2^+$ system. In the Finkelstein–Horowitz approximation [21], the $r$-space wavefunction of the system is given by

$$\Psi(\boldsymbol{r}) = (2 + 2S)^{-1/2}\{1s_A(\boldsymbol{r}) + 1s_B(\boldsymbol{r})\}, \tag{18a}$$

$$1s_A(\boldsymbol{r}) = (\zeta^3/\pi)^{1/2} \exp(-\zeta|\boldsymbol{r} - \boldsymbol{R}_A|), \tag{18b}$$

where $S$ is the overlap integral and $\boldsymbol{R}_A$ the position of nucleus $A$. The exponent $\zeta = \zeta(R)$ is optimized at every internuclear distance $R$ $[\equiv|\boldsymbol{R}_A - \boldsymbol{R}_B|]$ and this guarantees the validity of the basic equation of the present approach. The $p$-space wavefunction corresponding to Eq. (18) is [14, 22]

$$\Psi(\boldsymbol{p}) = (2 + 2S)^{-1/2}\{1s_A(\boldsymbol{p}) + 1s_B(\boldsymbol{p})\}, \tag{19a}$$

$$1s_A(\boldsymbol{p}) = \exp(-i\boldsymbol{p}\cdot\boldsymbol{R}_A)1s(\boldsymbol{p}), \tag{19b}$$

where $1s(\boldsymbol{p})$ is given by Eq. (10a). We then have the radial momentum density

$$I(p)=\{2^5\pi^{-1}\zeta^5(1+S)^{-1}\}p^2(p^2+\zeta^2)^{-4}\{1+(\sin pR)/pR\}. \tag{20}$$

For diatomic systems, the uniform scaling factor $s$ can be replaced by the internuclear distance $R$. Therefore, Eq. (7b) is rewritten as

$$E=-\int dp\,(p^2/2)\hat{I}(p), \tag{21a}$$

$$\hat{I}(p)=(1/R)\int_0^R dR'I(p;R'). \tag{21b}$$

Since the $R$-dependence of $\zeta_{\text{opt}}(R)$ is not simple, the integration in Eq. (21) has been numerically carried out using the Gauss formula. In Fig. 1, the resultant $\hat{I}(p)$ is depicted for several $R$ together with the original $I(p)$. In the $R$-range examined, $I(p)$ and $\hat{I}(p)$ show gradual migration of momentum density from large $p$-region to small $p$-region. (Note that $\int_0^\infty dp\,I(p)=\int_0^\infty dp\,\hat{I}(p)=N$.) This is contraction of momentum density. Correspondingly, $T$ and $-E$ monotonously decrease as $R$ increases. The proposed guiding principle of contraction and expansion for the behaviour of momentum density [11] is also valid in the present case. The electronic energies obtained from Eq. (21a) are summarized in Table 1. The results agree with those of the direct calculation. In Table 1, an energy decomposition is also given which results from the partitioning of $I(p)$ into one- and two-center parts. Of the two components, the contribution of the one-center part becomes large as $R$ increases. This is mainly due to the enlargement of the space of electron movement which causes a decrease in the kinetic pressure of the two-center part. The two-center part is also the predominant origin of the contraction observed in Fig. 1.

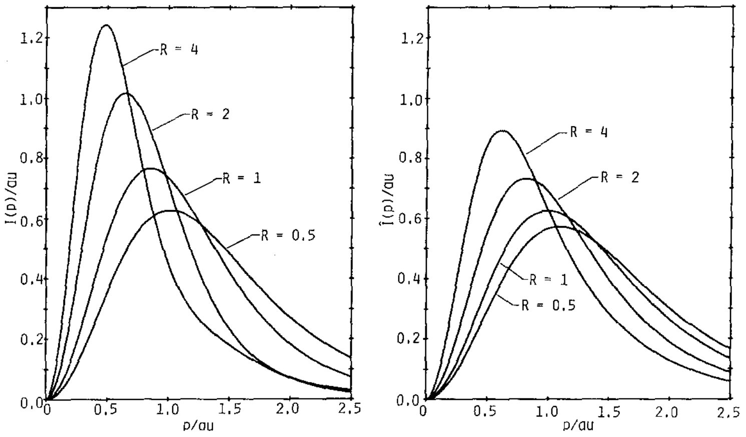

**Fig. 1.** Radial momentum densities $I(p)$ and $\hat{I}(p)$ for the $1s\sigma_g$ state of $H_2^+$ system

**Table 1.** Ground-state electronic energy of $H_2^+$ system based on the Finkelstein–Horowitz wavefunction[a]

| | $-E$/a.u. | | | |
|---|---|---|---|---|
| $R$/a.u. | Eq. (21) | | | Direct calculation |
| | One-center | Two-center | Total | |
| 0.5 | 0.92872 (54) | 0.80304 (46) | 1.73176 | 1.73176 |
| 1 | 0.84456 (59) | 0.59644 (41) | 1.44100 | 1.44100 |
| 2 | 0.71956 (66) | 0.36695 (34) | 1.08651 | 1.08651 |
| 3 | 0.64231 (72) | 0.25547 (28) | 0.89778 | 0.89778 |
| 4 | 0.59511 (76) | 0.19222 (24) | 0.78733 | 0.78733 |
| 5 | 0.56666 (79) | 0.15255 (21) | 0.71921 | 0.71921 |

[a] Values in parentheses mean percent ratios.

### 3.2. *Vibrational Energy*

As a simple example of the energy change accompanied by nuclear isotope substitution, we may consider the vibrational energy of diatomic molecules based on the momentum density.

Under appropriate approximation, the problem of diatomic vibration is reduced to the problem of a one-dimensional harmonic oscillator, whose ground-state wavefunction and energy are (see e.g. [23])

$$\Phi(X) = (\mu k/\pi^2)^{1/8} \exp[-(\mu k)^{1/2} X^2/2], \tag{22a}$$

$$W = (k/\mu)^{1/2}/2. \tag{22b}$$

Here, $X \equiv R - R_e$, $\mu[\equiv M_A M_B/(M_A + M_B)]$ is the reduced mass, and $k$ $[\equiv (d^2E/dR^2)_{R=R_e}]$ the force constant. Note that though Eq. (22a) has the same form as the approximate wavefunction $1s_{\text{app}}$ employed in Sect. 3.1.1. its mass-dependence is different. After evaluating the momentum wavefunction and density, which are similar to Eq. (13), we finally obtain

$$\begin{aligned}\hat{\rho}(P) &= \int_{\mu_1}^{\mu_2} d\mu\, \mu^{-2} \rho(P;\mu) \\ &= 2\pi^{-1/2} k |P|^{-5} \{\gamma(5/2, [k\mu_1]^{-1/2} P^2) - \gamma(5/2, [k\mu_2]^{-1/2} P^2)\},\end{aligned} \tag{23a}$$

$$\begin{aligned}\Delta W &= -\int_{-\infty}^{+\infty} dP (P^2/2) \hat{\rho}(P) \\ &= [(k/\mu_2)^{1/2} - (k/\mu_1)^{1/2}]/2,\end{aligned} \tag{23b}$$

where $\gamma(a, x)$ is the incomplete gamma function. Eq. (23b) correctly predicts the energy change of isotopic substitution, in accordance with the direct use of Eq. (22b). Since $W \propto \mu^{-1/2}$, we can also calculate $W$ itself from Eq. (23) by choosing $\mu_1 = \infty$ and $\mu_2 = \mu$.

## 4. Summary

Based on the integrated H–F theorem, we have discussed a method which rigorously connects the energy and the momentum electron density. Taking the electron mass as a parameter, we have derived an energy–density formula in $p$-space which corresponds to the Wilson–Frost formula in $r$-space. It has been shown that the scaled wavefunction is a floating function with respect to the parameter $m$, and that the present result of the energy–momentum density equation is equivalent to one of the previous results obtained from the virial theorem. Application of the integral H–F theorem has also been examined. Several examples have been given which illustrate the use of momentum density for the calculation and interpretation of energy.

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