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Short Communication

Energy–Density Relations in Momentum Space

II. Generalization

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Rigorous relations are derived between the electronic energy and the electron momentum density of a molecular system whose Hamiltonian takes the form of $g(\lambda)T(\{\boldsymbol{r}\})+h(\lambda)V(\{\boldsymbol{r}\};\{\boldsymbol{R}\})$ and depends on a parameter λ.

Key words: Momentum density – Compton profile – Hellmann–Feynman theorem – Scaling relation.

1. Introduction

In a previous paper [1], we have derived rigorous relations between the electronic energy and the electron momentum density of a molecular system based on the integrated Hellmann–Feynman theorem [2] with respect to the electron mass. We here generalize the previous results of energy–momentum density relations for the case where a parameter λ is embedded in the kinetic and potential energy parts through arbitrary functions $g(\lambda)$ and $h(\lambda)$. We also derive energy expressions when the Compton profile (see e.g. [3]) or the autocorrelation function (see e.g. [4]) is known. Use of scaling relations is discussed. Though we confine ourselves to the electronic problem, the results have a straightforward applicability to the nuclear problem (see [1]). Atomic units are used throughout this paper.

2. Energy Differences from Momentum Density and Related Quantities

Let us consider an N-electron molecular system whose electronic Hamiltonian takes the form of

$$H'(\{\boldsymbol{r}\};\{\boldsymbol{R}\},\lambda)=g(\lambda)T(\{\boldsymbol{r}\})+h(\lambda)V(\{\boldsymbol{r}\};\{\boldsymbol{R}\}), \tag{1}$$

where T and V are the parameter-independent parts of the kinetic and Coulombic potential energy operators respectively, and $\{\boldsymbol{r}\}$ and $\{\boldsymbol{R}\}$ denote the sets of position vectors of the electrons and the nuclei. The functions $g(\lambda)$ and $h(\lambda)$ may be regarded as completely fictitious functions or as some realistic scaling functions for the electron mass, Planck constant, electronic charge, and so on.

Since Eq. (1) is rewritten as

$$H'(\{\boldsymbol{r}\};\{\boldsymbol{R}\},\lambda)=h(\lambda)H(\{\boldsymbol{r}\};\{\boldsymbol{R}\},\lambda), \tag{2a}$$

$$H(\{\boldsymbol{r}\};\{\boldsymbol{R}\},\lambda)=f(\lambda)T(\{\boldsymbol{r}\})+V(\{\boldsymbol{r}\};\{\boldsymbol{R}\}), \tag{2b}$$

$$f(\lambda)=g(\lambda)/h(\lambda), \tag{2c}$$

the energy $E'(\{\boldsymbol{R}\},\lambda)$ corresponding to Hamiltonian H' is obtained from the knowledge of the energy $E(\{\boldsymbol{R}\},\lambda)$ corresponding to the new Hamiltonian H through the relation $E'(\{\boldsymbol{R}\},\lambda)=h(\lambda)E(\{\boldsymbol{R}\},\lambda)$. We assume that $f(\lambda)$ is a real continuous function and specifically $f(\lambda)=1$ represents the actual system. According to the method described previously [1], we can obtain a relation between E and the momentum density as follows.

The parameter λ appears only linearly to the kinetic energy operator in the Hamiltonian H (Eq. (2b)). Then using the momentum representation, we obtain

$$\Delta E=E(\lambda_2)-E(\lambda_1) \tag{3a}$$

$$=\int_{\lambda_1}^{\lambda_2} d\lambda\,[df(\lambda)/d\lambda]\left[\int d\boldsymbol{p}\,(p^2/2)\rho(\boldsymbol{p};\lambda)\right] \tag{3b}$$

$$=\int_{f_1}^{f_2} df\left[\int d\boldsymbol{p}\,(p^2/2)\rho(\boldsymbol{p};f)\right] \tag{3c}$$

from the integrated Hellmann–Feynman theorem with respect to the parameter λ. Here the other parameter $\{\boldsymbol{R}\}$ is omitted for the sake of simplicity. $\rho(\boldsymbol{p})$ is the momentum density of the system specified by the Hamiltonian H, $\boldsymbol{p}$ the momentum vector of an electron, and $p=|\boldsymbol{p}|$. $f_1=f(\lambda_1)$ and $f_2=f(\lambda_2)$. Eq. (3) implies that ΔE is free from the functional form of f, and we can treat the function f as a single parameter. As discussed in a previous paper [1], ΔE becomes the energy itself, if the range of the integration in Eq. (3c) is chosen to be $f_1=\infty$ and $f_2=1$.

Exchanging the order of the integrations of Eq. (3c), we get

$$\Delta E=\int d\boldsymbol{p}\,(p^2/2)\hat{\rho}(\boldsymbol{p}), \qquad \hat{\rho}(\boldsymbol{p})=\int_{f_1}^{f_2} df\,\rho(\boldsymbol{p};f), \tag{4}$$

which shows that the modified momentum density $\hat{\rho}$ governs the energy. When the radial momentum density $I(p)$ $[=\int_0^{2\pi} d\phi_p \int_0^{\pi} d\theta_p\, p^2 \sin\theta_p\, \rho(\boldsymbol{p})]$ is used, Eq.

(4) is simplified to

$$\Delta E = \int_0^\infty dp\,(p^2/2)\hat{I}(p), \qquad \hat{I}(p) = \int_{f_1}^{f_2} df\, I(p;f). \tag{5}$$

Using the isotropic Compton profile $J(q)$ $[=(1/2)\int_{|q|}^{\infty} dp\, p^{-1} I(p)]$ and the directional Compton profiles $J_i(p_i)$ $[=\int_{-\infty}^{+\infty} dp_{i'}\, dp_{i''}\, \rho(\boldsymbol{p})]$ $(i, i', i'' = x, y, z)$, we can rewrite Eqs. (4) and (5) as follows.

$$\Delta E = \int_0^\infty dq\,(3q^2)\hat{J}(q), \qquad \hat{J}(q) = \int_{f_1}^{f_2} df\, J(q;f). \tag{6}$$

$$\Delta E = \sum_{i=x,y,z} \int_{-\infty}^{+\infty} dp_i\,(p_i^2/2)\hat{J}_i(p_i), \qquad \hat{J}_i(p_i) = \int_{f_1}^{f_2} df\, J_i(p_i;f). \tag{7}$$

When the Fourier transform $B(\boldsymbol{r})$ $[=\int d\boldsymbol{p}\, \exp(-i\boldsymbol{p}\boldsymbol{r})\rho(\boldsymbol{p})]$ of $\rho(\boldsymbol{p})$ and its spherical average $b(r)$ $[=(4\pi)^{-1}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\, \sin\theta\, B(\boldsymbol{r})]$ are applied, we also obtain

$$\Delta E = -(1/2)[\hat{B}^{(2,0,0)}(\boldsymbol{0}) + \hat{B}^{(0,2,0)}(\boldsymbol{0}) + \hat{B}^{(0,0,2)}(\boldsymbol{0})],$$

$$\hat{B}(\boldsymbol{r}) = \int_{f_1}^{f_2} df\, B(\boldsymbol{r};f), \tag{8}$$

$$\Delta E = -(3/2)\hat{b}^{(2)}(0), \qquad \hat{b}(r) = \int_{f_1}^{f_2} df\, b(r;f), \tag{9}$$

where $\hat{B}^{(l,m,n)}(\boldsymbol{r}) = \partial^{l+m+n}\hat{B}(\boldsymbol{r})/(\partial x^l \partial y^m \partial z^n)$ and $\hat{b}^{(n)}(r) = d^n\hat{b}(r)/dr^n$. It may be a merit of the use of $B(\boldsymbol{r})$ and $b(r)$ that $B(\boldsymbol{r})$ is the autocorrelation function of the position wave function and reduces to the overlap integral within the independent particle model and the natural orbital expansion [4]. Eqs. (8) and (9) result from the fact that the second moment of momentum is proportional to the second gradient of the autocorrelation function at the origin [5, 6]. We note that in Eqs. (7) and (8), ΔE is separated into the three directional components.

3. Use of Scaling Relations

In the preceding section, we have derived a relation between the energy change and the momentum density by considering a fictitious process where the parameter f varies from f_1 to f_2. However, we can obtain the required modified quantities from the result for the real system ($f = 1$) by recalling the fact that the momentum density corresponding to the Hamiltonian H (Eq. (2b)), for example, satisfies the scaling relation $\rho(\boldsymbol{p};\{\boldsymbol{R}\},f) = f^3\rho(f\boldsymbol{p};\{f^{-1}\boldsymbol{R}\},1)$. Namely, by the use of scaling relations, the six modified quantities appeared in eqs. (4)–(9)

are rewritten as

$$
\begin{aligned}
\hat{\rho}(\boldsymbol{p};\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, f^3 \rho(f\boldsymbol{p};\{f^{-1}\boldsymbol{R}\},1),\\
\hat{I}(p;\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, fI(fp;\{f^{-1}\boldsymbol{R}\},1),\\
\hat{J}(q;\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, fJ(fq;\{f^{-1}\boldsymbol{R}\},1),\\
\hat{J}_i(p_i;\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, fJ_i(fp_i;\{f^{-1}\boldsymbol{R}\},1), \qquad i=x,y,z,\\
\hat{B}(\boldsymbol{r};\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, B(f^{-1}\boldsymbol{r};\{f^{-1}\boldsymbol{R}\},1),\\
\hat{b}(r;\{\boldsymbol{R}\}) &= \int_{f_1}^{f_2} df\, b(f^{-1}r;\{f^{-1}\boldsymbol{R}\},1),
\end{aligned}
\tag{10}
$$

where the geometry dependence has been explicitly given. The right-hand-sides of the above equations mean the process of configurational change in the real system since the integrands depend on $\{f^{-1}\boldsymbol{R}\}$.

Fig. 1a depicts schematically the scaling relation in momentum space. The fictitious process which we have considered in Sect. 2 is represented by the vertical arrow F_1F_2. When the scaling relation is applied, F_1F_2 is projected to the arrow $F'_1F'_2$ along the hyperbola $st=1$ on the plane $f=1$. Simultaneously, the scaling factors for the geometry $\{\boldsymbol{R}\}$ and the momentum $\{\boldsymbol{p}\}$ are introduced. In the special case of atoms, the relation becomes a projection on the f–t plane ($s=0$). Fig. 1b shows the scaling relation in position space. The fictitious process

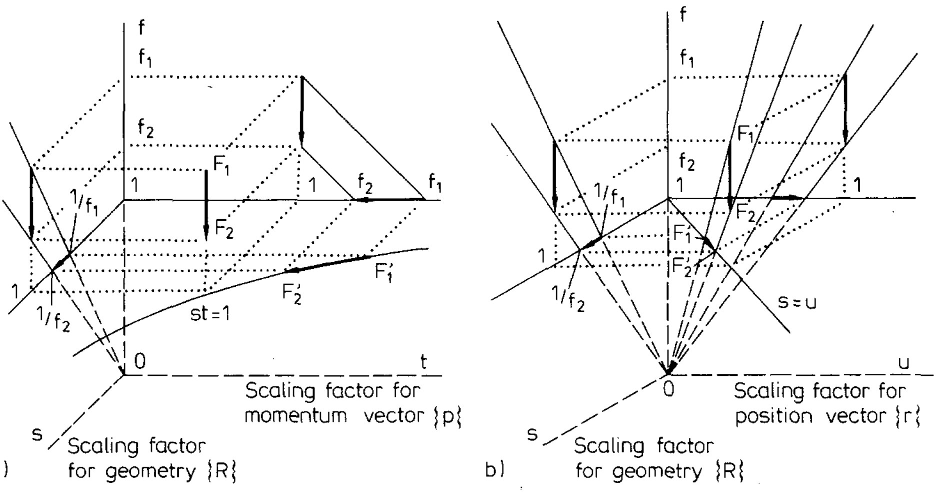

Fig. 1. Schematic representation of scaling relations. (**a**) Momentum space. (**b**) Position space

F_1F_2 is projected to the arrow $F'_1F'_2$ along the straight line $s = u$ on the plane $f = 1$. Since the scaling factor for the geometry $\{\boldsymbol{R}\}$ is identical to that for the electronic coordinates $\{\boldsymbol{r}\}$, the process $F'_1F'_2$ represents a uniform scaling process. The result reflects the fact [1] that the integrated Hellmann–Feynman theorem with respect to f is equivalent to the virial theorem for a uniform scaling process [7]. This point was also used by Frost and Lykos [8] in their derivation of the virial theorem from the Hellmann–Feynman theorem.

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