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Energy-density relations in momentum space. III. Variational aspect

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A variational formula for the momentum density is derived by using the Hellmann–Feynman theorem and by introducing a reference system whose Hamiltonian differs only in the kinetic energy part from that of the original system. As simple applications of the present results, the reduced mass correction and the relativistic correction for the hydrogen-like atom are discussed.

Key words: Variational formula—momentum density—Hellmann–Feynman theorem

1. Introduction

In a previous paper [1], we have derived rigorous relations between the energy and the electron density in momentum space based on the integrated Hellmann–Feynman theorem where the electron mass m is taken to be a parameter. Succeedingly [2], these results have been generalized to the case where the kinetic and potential energy operators depend on a parameter λ through arbitrary functions $g(\lambda)$ and $h(\lambda)$, respectively.

In the present paper, we study a variational formula for the momentum density following the idea of Nakatsuji and Parr [3] (see also footnote 4 of Ref. [4]). Namely, we derive a variational relation (variational integrated Hellmann–Feynman formula) for the momentum density on the basis of the energy-momentum density relations given in previous papers [1, 2]. For this purpose, we introduce a reference system (referred to as β system) whose potential energy operator is same as but the kinetic energy operator is different from those of the original system (referred to as α system), respectively. In this variational formula,

a parameter which is included in the kinetic energy operator and the momentum density of the β system plays a role of variational parameter. As a result, the formula has a restriction in practical applications, as the formula for the position density has [3], that we need to know the correct momentum density for the β system in advance. Therefore, the first application for the reduced mass effect (Sect. 3.1) is an example of simple verification of variational formula and it will not have much advantage from practical viewpoint. However, the problem of an approximate relativistic correction shown in Sect. 3.2 may illustrate that the present method constitutes one of possible methods to estimate the relativistic correction from the usual non-relativistic results. Atomic units are used in this paper.

2. Variational formula

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

$$H(\alpha) = T(\alpha) + V, \tag{1a}$$

including a parameter α. $T(\alpha)$ is the electronic kinetic energy operator and V the (α-independent) potential energy operator. This original system is called α system. We now introduce a reference (β) system having the electronic Hamiltonian

$$H'(\beta) = T'(\beta) + V, \tag{1b}$$

where β is another parameter. Namely, the β system has the same potential energy operator as the α system but has a different kinetic energy operator. If the correct energies and wave functions for the α and β systems are denoted by $E(\alpha)$, $\Psi(\alpha)$ and $E'(\beta)$, $\Psi'(\beta)$, respectively, we obtain

$$\begin{aligned}\langle\Psi(\alpha)|H(\alpha)|\Psi(\alpha)\rangle &\leq \langle\Psi'(\beta)|H(\alpha)|\Psi'(\beta)\rangle \\ &= \langle\Psi'(\beta)|H'(\beta) + T(\alpha) - T'(\beta)|\Psi'(\beta)\rangle,\end{aligned} \tag{2a}$$

from the Ritz variational principle. That is,

$$\begin{aligned}E(\alpha) &\leq \tilde{E}(\alpha;\beta) \\ &= E'(\beta) + \langle\Psi'(\beta)|T(\alpha) - T'(\beta)|\Psi'(\beta)\rangle.\end{aligned} \tag{2b}$$

If we use the momentum representation and substitute

$$T(\alpha) = \sum_{i=1}^{N} t(\boldsymbol{p}_i;\alpha), \qquad T'(\beta) = \sum_{i=1}^{N} t'(\boldsymbol{p}_i;\beta), \tag{3}$$

into Eq. (2b), then Eq. (2b) can be rewritten as

$$\begin{aligned}E(\alpha) &\leq \tilde{E}(\alpha;\beta) \\ &= E'(\beta) + \int [t(\boldsymbol{p};\alpha) - t'(\boldsymbol{p};\beta)]\rho'(\boldsymbol{p};\beta)\, d\boldsymbol{p},\end{aligned} \tag{2c}$$

where $\rho'(\boldsymbol{p};\beta)$ denotes the (three-dimensional) momentum density for the β system. We can regard Eq. (2c) as a momentum representation [5] of the Hohenberg–Kohn theorem [6].

Since $E'(\beta)$ can be expressed as [1, 2]

$$E'(\beta) = E'(\beta_0) + \int \left\{ \int_{\beta_0}^{\beta} [\partial t'(\boldsymbol{p};\beta')/\partial\beta'] \rho'(\boldsymbol{p};\beta')\, d\beta' \right\} d\boldsymbol{p}, \tag{4}$$

in terms of the momentum density, we finally obtain

$$\begin{aligned} E(\alpha) &\leq \tilde{E}(\alpha;\beta) \\ &= E'(\beta_0) + \int \left\{ \int_{\beta_0}^{\beta} [\partial t'(\boldsymbol{p};\beta')/\partial\beta'] \rho'(\boldsymbol{p};\beta')\, d\beta' \right. \\ &\quad \left. + [t(\boldsymbol{p};\alpha) - t'(\boldsymbol{p};\beta)] \rho'(\boldsymbol{p};\beta) \right\} d\boldsymbol{p}. \end{aligned} \tag{5a}$$

Although there remains the freedom for the choice of β_0, it is convenient to choose β_0 so as to $E'(\beta_0) = 0$ [1, 2]. Eq. (5a) constitutes a variational relation for the α system based on the momentum density $\rho'(\boldsymbol{p};\beta)$ of the β system, and β plays a role of the variational parameter. Namely, from the condition of $\partial\tilde{E}(\alpha;\beta)/\partial\beta = 0$, the best energy and momentum density are derived for the α system. When we use the result [1] from the integral Hellmann–Feynman theorem [7, 8], instead of Eq. (4), we obtain a different formula (variational integral Hellmann–Feynman formula)

$$\begin{aligned} E(\alpha) &\leq \tilde{E}(\alpha;\beta) \\ &= E'(\beta_0) + \int \{ [t'(\boldsymbol{p};\beta) - t'(\boldsymbol{p};\beta_0)][\tau'(\boldsymbol{p};\beta_0,\beta)/S'(\beta_0,\beta)] \\ &\quad + [t(\boldsymbol{p};\alpha) - t'(\boldsymbol{p};\beta)] \rho'(\boldsymbol{p};\beta) \}\, d\boldsymbol{p}, \end{aligned} \tag{6}$$

where τ' and S' are respectively the transition momentum density and transition overlap for the β system. However Eq. (6) is more complicated than Eq. (5a) in that the former requires both of ρ' and τ'. We therefore proceed with our following discussion using Eq. (5a).

The calculation of $\tilde{E}(\alpha;\beta)$ based on Eq. (5a) needs the kinetic energy operators t and t' and the momentum density ρ' be specified. Since the kinetic energy operator is usually a function of $p = |\boldsymbol{p}|$, Eq. (5a) can be simplified as follows,

$$\begin{aligned} E(\alpha) &\leq \tilde{E}(\alpha;\beta) \\ &= E'(\beta_0) + \int_0^{\infty} \left\{ \int_{\beta_0}^{\beta} [\partial t'(p;\beta')/\partial\beta'] I'(p;\beta')\, d\beta' \right. \\ &\quad \left. + [t(p;\alpha) - t'(p;\beta)] I'(p;\beta) \right\} dp, \end{aligned} \tag{5b}$$

where $I'(p;\beta) \equiv p^2 \int_0^{2\pi} \{ \int_0^{\pi} \rho'(\rho;\beta) \sin\theta_p\, d\theta_p \}\, d\phi_p$ is the radial momentum density for the β system. When the relations between the radial momentum density $I(p)$

and the isotropic Compton profile $J(q)$ (see e.g. [9]),

$$J(q)=(1/2)\int_{|q|}^{\infty} p^{-1}I(P)\,dp, \qquad I(p)=-2p[dJ(p)/dp], \tag{7}$$

are employed, Eq. (5b) is rewritten by using $J(q)$. In addition, we can also derive a variational formula in terms of the directional Compton profiles $J_x(p_x)$, $J_y(p_y)$, and $J_z(p_z)$ [2], if the kinetic energy operator is an additive sum of the directional components.

Eq. (5) is an exact variational relation for the α system and it applies not only to the electronic problem but also to the nuclear problem, though a priori knowledge about the β system is required. Since the α and β systems differ only in their kinetic energy operators, to solve the β system may be a problem of the same level as to solve the α system directly. Quite the same has been pointed out in position space [3]. In this sense, the applicability of the present results is limited.

3. Illustration

3.1. Reduced mass correction

For the hydrogen-like atom, let us consider the problem of taking into account the effect of the nuclear mass M using the reduced mass $\mu[=mM/(m+M)$ with m being the electron mass] (α system). The β system is the system of $M=\infty$. This problem is an example that the known results are correctly reproduced from the variational formula derived in the previous section, because $H(\mu)=H'(\mu)$ and $\rho(\mu)=\rho'(\mu)$.

The momentum wave function for the state specified by the quantum numbers (n, l, m_l) of the hydrogen-like atom with the nuclear charge Z is given in Refs. [10–13]. Then, the radial momentum density of the β system containing the electron mass m as a parameter is given by

$$I'_{nl}(p, m)=p^2[F_{nl}(p; m)]^2, \tag{8a}$$

$$\begin{aligned} F_{nl}(p; m)=&(mZ)^{-3/2}\{(2/\pi)[(n-l-1)!/(n+l)!]\}^{1/2} \\ &\times n^2 2^{2l+2} l!(np/mZ)^l[(np/mZ)^2+1]^{-(l+2)} \\ &\times C^{l+1}_{n-l-1}([(np/mZ)^2-1]/[(np/mZ)^2+1]), \end{aligned} \tag{8b}$$

where $C^{\alpha}_{N}(x)$ denotes the Gegenbauer polynomial (see e.g. [14]). Note that I'_{nl} is independent of the quantum number m_l. Eq. (5b) therefore becomes

$$\begin{aligned} E(\mu) &\le \tilde{E}(\mu; m) \\ &= E'(m_0)+\int_0^{\infty}\left\{\int_{m_0}^{m}(-p^2/2m'^2)I'_{nl}(p; m')\,dm'\right. \\ &\quad \left.+[(p^2/2\mu)-(p^2/2m)]I'_{nl}(p; m)\right\}dp, \end{aligned} \tag{9a}$$

where $E'(m_0)$ equals to $-m_0Z^2/(2n^2)$. The integrals appearing on the right-hand-side of Eq. (9a) are essentially the kinetic energy integrals which are immediately obtained from the virial theorem. The result is

$$\tilde{E}(\mu; m) = -(\mu Z^2/2n^2)[2(m/\mu)-(m/\mu)^2]$$
$$= (\mu Z^2/2n^2)[(m/\mu)-1]^2-(\mu Z^2/2n^2). \tag{9b}$$

Namely, $\tilde{E}(\mu: m)$ depends parabolically on the variational parameter m and it takes a minimum value $-(\mu Z^2/2n^2)$ at $m=\mu$. This is the correct result, as expected. Similar argument holds for the nuclear isotope effect.

3.2. Relativistic correction

When the approximate relativistic correction which accounts for the change of the electron mass with velocity is included, the kinetic energy operator is expressed as [15, 16]

$$t(p; m) = (p^2/2m)-(p^4/8m^3c^2), \tag{10}$$

where c is the velocity of light. Taking again the hydrogen-like atom as an example, we variationally obtain approximate energy and momentum density of the relativistic system (α system), which has the kinetic energy operator of Eq. (10), by using the non-relativistic result (β system) as a reference. For simplicity we write the electron mass in the β system as β. From Eqs. (5b) and (8), $\tilde{E}$ results in

$$\tilde{E}(m; \beta) = -(mZ^2/2n^2)\{2(\beta/m)-(\beta/m)^2$$
$$+(Z/2cn)^2[(8n-6l-3)/(2l+1)](\beta/m)^4\}, \tag{11}$$

where

$$\int_0^\infty p^2 I'_{nl}(p; \beta)\, dp = (\beta Z)^2/n^2, \tag{12a}$$

$$\int_0^\infty p^4 I'_{nl}(p; \beta)\, dp = [(\beta Z)^4/n^4][(8n-6l-3)/(2l+1)], \tag{12b}$$

have been used (see Refs. [14, 17] for the integrals involving the Gegenbauer polynomials). From the condition of $\partial\tilde{E}(m; \beta)/\partial\beta = 0$, the value of the parameter β which minimizes $\tilde{E}(m; \beta)$ of Eq. (11) is approximately,

$$\beta_{\min} \simeq \{1+2(Z/2cn)^2[(8n-6l-3)/(2l+1)]\}m. \tag{13a}$$

Eq. (13a) is correct to terms varying as c^{-2}. Then, the corresponding relativistic energy becomes

$$\tilde{E}_{\min} = \tilde{E}(m; \beta_{\min}) \simeq -(mZ^2/2n^2)\{1+(Z/2cn)^2[(8n-6l-3)/(2l+1)]\}. \tag{13b}$$

Recalling the fact that m (or β) plays a role of the orbital exponents in the momentum density [1], we see in Eq. (13) that the relativistic correction of Eq. (10) contracts the momentum density and lowers the energy. It is also clear that

the degree of contraction and lowering becomes larger with increasing Z and decreasing n. For given Z and n, the effect is smaller for larger $l(\leq n-1)$.

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