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Position moments linearly averaged over the wave function. II

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In a very recent paper,[1] it has been shown that there exists a set of relations between position moments linearly averaged over the wave function. These relations constitute a necessary condition for the true wave function and they provide a sensitive and convenient criterion to assess the accuracy of approximate wave functions. The zero momentum energy formula[2,3] or its modification[4] follows from the simplest case of the relations.

In the present note, we further generalize the above discussion and show that there also exists a set of relations between position moments linearly averaged over the wave function *in a finite domain*. The present results will be helpful to understand the structure of the Schrödinger equation in a nontrivial manner. The simplest case may be applied as a regional form of the zero momentum energy expression which measures the *regional accuracy* of wave functions.

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Let us consider the $3N$-dimensional (exponential) Fourier transformation of the N-electron position–space Schrödinger equation in a finite domain D. After integration by parts of the kinetic energy term, we obtain the following equation:

$$\begin{aligned} E\,[\exp(-i\mathbf{p}\cdot\mathbf{r})]_D &= [\exp(-i\mathbf{p}\cdot\mathbf{r})V(\mathbf{r})]_D + (p^2/2)[\exp(-i\mathbf{p}\cdot\mathbf{r})]_D \\ &\quad - (1/2)\sum_{j=1}^{3N}\left\{\left[\exp(-i\mathbf{p}\cdot\mathbf{r})\frac{\partial}{\partial r_j}\right]_{D_j} \right. \\ &\quad \left. + ip_j[\exp(-i\mathbf{p}\cdot\mathbf{r})]_{D_j}\right\}, \end{aligned} \tag{1}$$

where

$$[f(\mathbf{r})]_D \equiv \int_D f(\mathbf{r})\Psi(\mathbf{r})\,d\mathbf{r}, \tag{2a}$$

$$[f(\mathbf{r})]_{D_j} \equiv \int_{D'} f(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r}'\Big|_{r_j=a_j}^{b_j}, \tag{2b}$$

which are *linear* averages over the position wave function $\Psi(\mathbf{r})$ in the domain D. In Eq. (1), E is the total energy, $V(\mathbf{r})$ the potential energy operator, and $\mathbf{r}\equiv\{\mathbf{r}_i\} = (r_1,r_2,\ldots,r_{3N})$ and $\mathbf{p}\equiv\{\mathbf{p}_i\} = (p_1,p_2,\ldots,p_{3N})$ represent the $3N$ Cartesian coordinates of the position and momentum vectors for the N electrons. $p^2/2 = \Sigma_{j=1}^{3N}(p_j^2/2)$ is the kinetic energy operator. (Atomic units are used throughout.) In Eq. (2b), primes denote the omission of the r_j term, and the domain D is assumed to be specified by the lower (a_j) and upper (b_j) limits for the individual Cartesian component r_j, i.e., $a_j \leqslant r_j \leqslant b_j$ or $D = [\mathbf{a},\mathbf{b}]$ where $\mathbf{a} = \{a_j\}$ and $\mathbf{b} = \{b_j\}$. If we set $D = (-\infty, +\infty)$, then each term of the summation on the right-hand side of Eq. (1) vanishes and Eq. (1) results in the Schrödinger equation in momentum space.

Now expanding all the $3N$ exponential functions appearing in Eq. (1) and comparing the coefficients of the term $\Pi_{n=1}^{3N} p_n^{k_n}$, we obtain a set of relations:

$$\begin{aligned} E\left[\prod_{n=1}^{3N} r_n^{k_n}\right]_D &= \left[\left(\prod_{n=1}^{3N} r_n^{k_n}\right)V(\mathbf{r})\right]_D \\ &\quad - (1/2)\sum_{j=1}^{3N}\left\{k_j(k_j-1)\left[r_j^{-2}\left(\prod_{n=1}^{3N} r_n^{k_n}\right)\right]_D\right\} \\ &\quad - (1/2)\sum_{j=1}^{3N}\left\{\left[\left(\prod_{n=1}^{3N} r_n^{k_n}\right)\frac{\partial}{\partial r_j}\right]_{D_j} \right. \\ &\quad \left. - k_j\left[r_j^{-1}\left(\prod_{n=1}^{3N} r_n^{k_n}\right)\right]_{D_j}\right\} \quad (k_n = 0,1,2,\ldots,K_n). \end{aligned} \tag{3}$$

Equation (3) represents general relations existing among the position moments linearly averaged over the wave function in the domain D. The upper bound K_n for the exponent k_n may or may not be finite depending on the linear integrability[1,5] of the position wave function $\Psi(\mathbf{r})$. The true wave function must satisfy all of these relations and hence Eq. (3) can be used as a criterion for assessing the accuracy of approximate wave functions. High sensitivity of the criterion of this kind (which is linear in the wave function error) has been already demonstrated.[1–4,6–8] For a special case of $D = (-\infty, +\infty)$, the last term on the right-hand side of Eq. (3) vanishes and the known results for an infinite domain[1] are reproduced.

If we put $k_n = 0$ and $(a_n,b_n) = (-\infty, +\infty)$ in Eq. (3) except for k_1 and (a_1,b_1), we obtain a set of single component relations:

$$\begin{aligned} E\,[r_1^{k_1}]_D &= [r_1^{k_1}V(\mathbf{r})]_D - (1/2)k_1(k_1-1)[r_1^{k_1-2}]_D \\ &\quad - (1/2)\left\{\left[r_1^{k_1}\frac{\partial}{\partial r_1}\right]_{D_1} - k_1[r_1^{k_1-1}]_{D_1}\right\} \\ &\qquad (k_1 = 0,1,2,\ldots,K_1), \end{aligned} \tag{4}$$

where r_1 can be replaced with any other component of the $3N$-dimensional vector $\mathbf{r}$. Equation (4) also constitutes a necessary condition for the true wave function. For the simplest case of $k_1 = 0$, Eq. (4) reduces to

$$E\,[1]_D = [V(\mathbf{r})]_D - (1/2)\left[\frac{\partial}{\partial r_1}\right]_{D_1}, \tag{5a}$$

from which we obtain

$$\begin{aligned} E_{zm}(a_1,b_1) &\equiv E_{zm}(D) \\ &= \left\{[V(\mathbf{r})]_D - (1/2)\left[\frac{\partial}{\partial r_1}\right]_{D_1}\right\}/[1]_D, \end{aligned} \tag{5b}$$

where a_1 and b_1 are so chosen that $[1]_D \neq 0$. Equation (5b) is a regional form of the zero momentum energy (ZME) formula. The original ZME expression assumes the integration over an infinite domain and the second term of the numerator of Eq. (5b) does not appear.[1,2] From this choice of the domain, however, the original ZME formula suffers a restriction to its applicability that the wave function should be spatially totally symmetric,[2–4] since otherwise the formula always results in an indeterminate 0/0 form. The proposed modification[4] avoids this difficulty by considering a higher moment linearly averaged over the wave function.

On the other hand, the present regional form of the ZME expression [Eq. (5b)] removes the indeterminate case by an appropriate choice of the integral domain D. More significantly, Eq. (5b) enables us to measure the accuracy of wave functions in some specific region of interest. The gradient term in Eqs. (5) accounts for the kinetic energy contribution at the boundary surface of the domain.

Use of Eq. (3) or (4), instead of Eq. (5a), allows us to derive a generalized form of the regional ZME formula, but its practical applications seem rather involved. For a particular case of $D \to 0$ or $\mathbf{b} \to \mathbf{a}$, all of these regional formulas reduce apparently to pointwise formulas. However, they are nothing but the original Schrödinger equation and the well-known local energy formula[9,10] in position–space. In this sense, the present regional ZME expressions give a bridge between the local energy and zero momentum energy formulas, which measure the pointwise and average accuracies, respectively.

A simple example to illustrate the use of the regional ZME formula [Eq. (5b)] will be an examination of a single s-type Gaussian approximation to the ground-state hydrogen atom. For the optimum exponent $\alpha = 8/9\pi$, the regional ZMEs are evaluated to be $-0.502\,941$, $-0.536\,496$, $-0.986\,802$, $-1.787\,996$, and $-2.916\,926$, respectively, for the regions $(a_1,b_1) = (0,1)$, $(1,2)$, $(2,3)$, $(3,4)$, and $(4,5)$, while the ZME (for an infinite region) is $-0.600\,211$. Comparison of these values together with the average and exact energies suggests that the regional ZME may be rather more sensitive to the asymptotic behavior than to the cusp behavior of wave functions.

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