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Previously, the zero momentum energy expression was proposed[1,2] as a sensitive criterion to assess the accuracy of approximate electronic wave functions. The expression is derived by considering the local energy[3,4] in momentum space and by taking its value at one special point, the momentum-space origin, where all the electron momenta vanish. Recently,[5] the limited applicability of the original zero momentum energy formula has been pointed out and a modification has been proposed to ensure its general utility. Applications to several atomic and molecular systems have revealed[1,2,5-8] that the zero momentum energy check is indeed a severe test of approximate wave functions compared with the ordinary check by the energy expectation value.

In the present article, we show that there exists a set of relations between position moments r^k averaged over the wave function $\Psi(\mathbf{r})$ not over $|\Psi(\mathbf{r})|^2$, where k is a *nonnegative* integer. The true wave function must satisfy all of these relations. The zero momentum energy expression[1,2] or its modification[5] arises from the simplest case of this set of relations.

Based on the N-electron Schrödinger equation either in position or momentum space, we obtain an equation

$$E[\exp(-i\mathbf{p}\cdot\mathbf{r})]$$
$$= [\exp(-i\mathbf{p}\cdot\mathbf{r})V(\mathbf{r})] + (p^2/2)[\exp(-i\mathbf{p}\cdot\mathbf{r})], \quad (1)$$

where E is the energy, $V(\mathbf{r})$ the potential energy operator, and $\mathbf{r} \equiv \{r_i\} = (r_1, r_2, ..., r_{3N})$ and $\mathbf{p} \equiv \{p_i\} = (p_1, p_2, ..., p_{3N})$ represent the $3N$ Cartesian coordinates of the position and momentum vectors for N electrons. $p^2/2 = \sum_{i=1}^{3N}(p_i^2/2)$ is the kinetic energy operator. (Atomic units are used throughout.) The symbol $[f(\mathbf{r})]$ is defined by

$$[f(\mathbf{r})] \equiv \int f(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r}, \quad (2)$$

which is a *linear* average over the position wave function $\Psi(\mathbf{r})$.

For the sake of simplicity, we first set all components of the vector $\mathbf{p}$ involved in Eq. (1) zero except for p_1, the x component of momentum vector $\mathbf{p}_1$ of the electron labeled 1. Then expanding the remaining exponential function $\exp(-ip_1r_1)$ and comparing the p_1^k terms on both sides of Eq. (1), we obtain a set of relations

$$E[r_1^k] = [r_1^k V(\mathbf{r})] - (1/2)k(k-1)[r_1^{k-2}]$$
$$(k = 0,1,2,...,K). \quad (3)$$

These are single component relations and r_1 can be replaced with any other component of the $3N$-dimensional vector $\mathbf{r}$. k runs over all *nonnegative* integers for which the above integrals are meaningful. The upper bound K may or may not be finite depending on the linear integrability of the position wave function $\Psi(\mathbf{r})$ and hence on the differentiability or smoothness of the counterpart momentum wave function $\Phi(\mathbf{p})$ [see Ref. 9].

A special case of Eq. (3) for $k = 0$ is

$$E = [V(\mathbf{r})]/[1] \quad (4a)$$

which is the original form[1,2] of the zero momentum energy expression provided $[1] \neq 0$. The modified zero momentum energy expression[5] is also derived as a particular case of Eq. (3): let κ be the smallest k for which $[r_1^k] \neq 0$. Then we have

$$E = [r_1^\kappa V(\mathbf{r})]/[r_1^\kappa], \quad (4b)$$

since $[r_1^{\kappa-2}] = 0$ by assumption.

In other words, the zero momentum energy expression[1,2] or its modification[5] is a single particular equation of the set (3), in which k is chosen to be the smallest integer with nonvanishing $[r_1^k]$. However, Eq. (3) constitutes a set of relations, *all* of which should be satisfied by the true wave function. When one adopts a single relation from this set as a criterion, a different choice of k may provide a measure of different level for the accuracy of approximate wave functions. Note that Eq. (3) is a necessary but not sufficient condition for the true wave function.

If we retain all components of $\mathbf{p}$ in Eq. (1), we can derive more general relations. Expanding all the $3N$ exponential functions and comparing the coefficients of the term $\prod_{i=1}^{3N} p_i^{k_i}$, we finally obtain a set of multicomponent relations

$$E\left[\prod_{i=1}^{3N} r_i^{k_i}\right] = \left[\left(\prod_{i=1}^{3N} r_i^{k_i}\right)V(\mathbf{r})\right]$$
$$- (1/2)\sum_{i=1}^{3N}\left\{k_i(k_i-1)\left[r_i^{k_i-2}\prod_{j \neq i}^{3N} r_j^{k_j}\right]\right\}$$
$$(k_i = 0,1,2,...,K_i) \quad (5)$$

for nonnegative integers k_i, which includes Eq. (3) as a special case. The relations (5) also constitute necessary conditions for the true wave function, and the discussion given for the single component relations applies as well.

The simplest example to illustrate the present results will be the ground-state hydrogen-like atom with $E = -Z^2/2$, where Z is nuclear charge. For $\Psi(\mathbf{r}) = \exp(-Zr)$ and $V(\mathbf{r}) = -Z/r$, the nonvanishing multicomponent moments are found to be

$$[x^{2i}y^{2j}z^{2k}] = \{8\pi(2i)!(2j)!(2k)!(i+j+k+1)!\}/$$
$$\{i!\,j!\,k!\,Z^{2(i+j+k)+3}\}, \quad (6a)$$

$$[x^{2i}y^{2j}z^{2k}V] = -\{4\pi(2i)!(2j)!(2k)!(i+j+k)!\}/$$

$$\{i\,!j\,!k\,!Z^{2(i+j+k)+1}\} \qquad (6b)$$

and hence Eq. (5) holds for any set of nonnegative integers i, j, and k. There is no upper bound in this case. Another example is the Kellner approximation[10] to the ground-state helium atom, for which the original zero momentum energy formula was not successful as a criterion.[1,2] For the Kellner wave function (i.e., a single product of the scaled hydrogenic $1s$ functions), the zero momentum energy [Eq. (4a)] coincides accidentally with the average energy $-2.847\,656$ and this approximate function has been considered[1,2] to satisfy the necessary condition exceptionally. However, if we apply Eq. (3) with $k = 2$, we obtain the value $-2.874\,023$ and the Kellner function does not satisfy the third relation of Eq. (3). This example illustrates that the use of a single relation can be misleading.

In summary, we have derived a set of relations between position moments linearly averaged over the wave function. These relations constitute necessary conditions for the true wave function. The use of the present results is discussed as criteria for the accuracy of wave functions with simple illustrations.

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