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Schrödinger equation in terms of linearly averaged position moments

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Linearily averaged position moment (LAPM) \( \{ R_{i}^{k} \} = \left\{ R_{1}^{k}, R_{2}^{k}, \ldots, R_{N}^{k} \right\} \) is defined as the linear (not quadratic) average of the position moment operator \( R_{i}^{k} \) over the \( N \)-electron wave function \( \Psi(\{ R_{j} \}) \), where \( \{ R_{j} \} \) are \( 3N \) Cartesian coordinates of electrons and \( \{ k_{j} \} \) are non-negative integers. When all the LAPM’s are well defined, it is shown that the Schrödinger equation is equivalent to a set of an infinite number of equations between LAPM’s involving the potential-energy operator. The kinetic energy operator does not appear. The spherical polar representation of the LAPM equation is also presented. Illustrations are given for simple one- and two-electron atoms, where the LAPM equation is applied to the determination of approximate wave functions and associated energies.

I. INTRODUCTION

Previously, the zero momentum energy expression has been proposed\(^{1-3} \) and applied\(^{1-5} \) as a sensitive criterion to assess the accuracy of approximate wave functions. The expression has been derived by the application of the local energy concept\(^{6,7} \) to the momentum-space Schrödinger equation: The equation to be satisfied at the momentum-space Schrödinger equation is equivalent to a set of an infinite number of equations between LAPM’s involving the potential-energy operator. The kinetic energy operator does not appear. The spherical polar representation of the LAPM equation is also presented. Illustrations are given for simple one- and two-electron atoms, where the LAPM equation is applied to the determination of approximate wave functions and associated energies.

II. FORMALISM

The \( N \)-electron Schrödinger equations in position and momentum spaces are written as

\[
( -\Delta/2 + V(r) - E) \Psi(r) = 0, \quad (2a)
\]

\[
(p^2/2 - E) \Phi(p) + \int W(p - p') \Phi(p') dp' = 0, \quad (2b)
\]

where \( r \equiv \{ r_{j} \} \) and \( p \equiv \{ p_{j} \} \) are position and momentum vectors of the electrons, respectively, and \( \Delta \equiv \sum_{j=1}^{N} \Delta_{j} \) and \( p^2 \equiv \sum_{j=1}^{N} |p_{j}|^2 \). The wave functions \( \Psi(r) \) and \( \Phi(p) \) and the potential-energy operators \( V(r) \) and \( W(p) \) are, respectively, pairs of the Fourier transforms:

\[
\Phi(p) = (2\pi)^{3N/2} \int \exp(-ir\cdot p) \Psi(r) \, dr, \quad (3a)
\]

\[
\Psi(r) = (2\pi)^{3N/2} \int \exp(+ir\cdot p) \Phi(p) \, dp, \quad (3b)
\]

\[
W(p) = (2\pi)^{-3N} \int \exp(-ir\cdot p) \, V(r) \, dr, \quad (4a)
\]

\[
V(r) = \int \exp(+ir\cdot p) \, W(p) \, dp, \quad (4b)
\]

where \( \Sigma_{j=1}^{N} r_{j}/p_{j} \).

Combining Eqs. (2)–(4), we obtain the Schrödinger equation in an intermediate representation:

\[
(p^2/2 - E) \left[ \exp(-ir\cdot p) \right] + \left[ \exp(-ir\cdot p) \, V(r) \right] = 0, \quad (5)
\]

where the square brackets stand for

\[
[f(r)] = \int f(r) \Psi(r) \, dr, \quad (6)
\]

which is a linear average of \( f(r) \) over the position wave function \( \Psi(r) \). We implicitly assume that the two integrals appearing in Eq. (5) do exist.
A. Cartesian representation

Now we expand the exponential function \( \exp(-ir\cdot p) \) in an absolutely convergent series:

\[
\exp(-ir\cdot p) = \sum_{j_0=0}^{\infty} (-i)^j \left( \frac{R_j}{p_{j_0}} \right)^j
\]

where \( \{R_j\} \) and \( \{p_{j_0}\} \) represent the 3N Cartesian coordinates of the position and momentum vectors of the \( N \) electrons. We assume all the LAPM's \( \Pi_{j_0}^N R_j \) and \( \Pi_{j_0}^N R_j V(r) \) exist and their linear combinations are well defined. Then we can exchange the integration and the summation when Eq. (7) is substituted into Eq. (5) where

\[
\text{as an alternative form of Eq. (5). For Eq. (8) to hold for any values of } k_j \text{, all the coefficients of } P^N_{\pm} \text{ appearing on the left-hand side of Eq. (8) must vanish;}
\]

\[
\frac{1}{2} \sum_{m=1}^{2N} k_m (k_m - 1) \left[ R^{-m} \prod_{j=1}^{N} R_j^k \right] + E \left[ \prod_{j=1}^{N} R_j^k \right] - \left[ \prod_{j=1}^{N} R_j^k V(r) \right] = 0,
\]

where \( k_j = 0,1,2,... \). Equation (9) represents a set of an infinite number of equations, and is equivalent to the Schrödinger equation provided that all the LAPM's and their linear combinations are well defined. It may be interesting to observe that in Eq. (9) the kinetic energy operator does not appear and its contribution is represented by the first term.

If we set \( k_j = k_i = m = k_i \equiv 0 \) in Eq. (9), we obtain a special form:

\[
\left( \pi \cdot \pi \right) \left[ R^{-m} \prod_{j=1}^{N} R_j^k \right] + E \left[ \prod_{j=1}^{N} R_j^k \right] - \left[ \prod_{j=1}^{N} R_j^k V(r) \right] = 0,
\]

which is a set of single-component equations and constitutes a subset of Eq. (9).

B. Spherical polar representation

When the system under consideration has a spherical symmetry, the use of the spherical polar coordinates is natural. The relation to be satisfied between the LAPM's in the spherical polar coordinates can be derived as follows.

We first invoke the plane-wave expansion\(^{11}\)

\[
\exp(-ip\cdot r_j) = 4\pi \sum_{l_j=0}^{\infty} \sum_{m_j=-l_j}^{l_j} \left( -i \right)^l Y_{lj}(p_j r_j) Y_{lj}(\Omega_j) Y_{lj}(\Omega_j),
\]

where \( (p_j, \Omega_j) \) and \( (r_j, \omega_j) \) are the spherical polar coordinates of the vectors \( p_j \) and \( r_j \), respectively. \( Y_{lj} \) is the usual spherical harmonic\(^{11}\) and \( j_l(z) \) is the spherical Bessel function of the first kind.\(^{12}\) Substituting Eq. (11) into the parent equation (5) and gathering the coefficients of the linearly independent term \( \Pi_{j_0}^N Y_{lj}(\Omega_j) \), we obtain

\[
\frac{1}{2} \left( \sum_{l=0}^{\infty} j_l(z) \right) \left[ \prod_{l=1}^{\infty} j_l(p_j r_j) Y_{lj}(\omega_j) \right] - E \left[ \prod_{l=1}^{\infty} j_l(p_j r_j) Y_{lj}(\omega_j) \right] + \left[ V(r) \prod_{l=1}^{\infty} j_l(p_j r_j) Y_{lj}(\omega_j) \right] = 0.
\]

Substitution of the expansion\(^{12}\) for \( j_l(z) \)

\[
\sum_{l=1}^{\infty} \left( -1 \right)^l (l + k) l! k! (2l + 2k + 1)! z^{2k},
\]

into Eq. (12) followed by comparison of the coefficients of \( \Pi_{j_0}^{2N} p_j^{l+2k} \) gives the desired result:

\[
\sum_{l=1}^{\infty} k_l (2l + 2k + 1) \left[ r^{-l-2} \prod_{j=1}^{\infty} r_j^{l+2k} Y_{lj}(\omega_j) \right] + E \left[ \prod_{j=1}^{\infty} r_j^{l+2k} Y_{lj}(\omega_j) \right] - \left[ V(r) \prod_{j=1}^{\infty} r_j^{l+2k} Y_{lj}(\omega_j) \right] = 0,
\]

where \( k_l = 0,1,2,...; l_i = 0,1,2,...; m_i = -l_i, -l_i + 1, ..., + l_i \) for \( i = 1,2,...,N \). Equation (14) is a set of LAPM equations in the spherical polar coordinates.

A special case of Eq. (14) for \( l_i = m_i = 0 \) (\( i = 1,2,...,N \)) reads

\[
\sum_{l=1}^{\infty} k_l (2l + 1) \left[ r^{-l-2} \prod_{j=1}^{\infty} r_j^{2k} \right] + E \left[ \prod_{j=1}^{\infty} r_j^{2k} \right] - \left[ V(r) \prod_{j=1}^{\infty} r_j^{2k} \right] = 0,
\]

since \( Y_{lj}(\omega_j) = (4\pi)^{-1/2} \). If we set \( k_l = k_i = m = k_i \equiv 0 \), Eq. (15) further reduces to a set of single-component equations

\[
k_l (2l + 1) \left[ r^{-l-2} \right] + E \left[ r^{2k} \right] - \left[ V(r) \right] = 0,
\]

which may compare with Eq. (10) in the Cartesian representation.
C. Discussion

Equation (9) may be considered as a projection of the position-space Schrödinger equation onto momentum space with the discrete Cartesian bases $\Pi_{j=1}^{\infty} P_j^l$ defined by a set of non-negative integers $\{k_j\}$. Similarly, Eq. (14) is regarded as a projection onto the spherical polar bases $\Pi_{j=1}^{\infty} P_{jl}^{\pi}$ given in the spherical polar coordinates. For a single-electron system $V(r)$, when a trial function includes some parameters as we determine $E$, we assume a radial function $R(r)$ of the form

$$R(r) = \sum_{l=0}^{\infty} a_l r^l \exp(-\xi r),$$

where $\xi = Z/n$. For a hydrogen-like atom with nuclear charge $Z$, Eq. (17) suggests that the wave function $\Psi(r)$ has the following form:

$$\Psi(r) = R(r) Y_{ij}^m(\omega).$$

When $V(r) = - Z/r$ (i.e., a hydrogen-like atom with nuclear charge $Z$), Eq. (17) suggests that the wave function $\Psi(r)$ has the following form:

$$\Psi(r) = R(r) Y_{ij}^m(\omega).$$

III. ILLUSTRATIVE APPLICATIONS

In the following, we apply the LAPM equation to (approximate) solutions of two simple systems, i.e., the hydrogen-like atom and the ground-state helium atom. In the former case, the correct wave function and the associated eigenenergy are completely reproduced. In the latter case, we discuss the property of approximate LAPM solutions using a simple trial function.

A. Hydrogen-like atom

For a single-electron system, the LAPM equation in the spherical polar coordinates [Eq. (14)] reads

$$k(2k + 2l + 1) \left[ r^{2k+1} \frac{\partial^2}{\partial r^2} Y_{ij}^m(\omega) \right] + E \left[ r^{2k+1} Y_{ij}^m(\omega) \right] - \left[ V(r)r^{2k+1} Y_{ij}^m(\omega) \right] = 0. \quad (17)$$

When $V(r) = - Z/r$ (i.e., a hydrogen-like atom with nuclear charge $Z$), Eq. (17) suggests that the wave function $\Psi(r)$ has the following form:

$$\Psi(r) = R(r) Y_{ij}^m(\omega).$$

Substituting Eq. (18) and the explicit form of $V(r)$ into Eq. (17), we obtain the radial LAPM equation:

$$k(2k + 2l + 1) \left[ r^{2k+1} \frac{\partial^2}{\partial r^2} \right] e^r + E \left[ r^{2k+1} e^r \right] + Z \left[ r^{2k+1} \right] e^r = 0, \quad (19)$$

where

$$[f(r)]_i = \int_0^\infty f(r) R(r) r^i dr. \quad (20)$$

If we assume a radial function $R(r)$ of the form

$$R(r) = \left( \sum_{l=0}^{n-1} a_l r^l \right) \exp(-\xi r), \quad (21)$$

Eq. (19) becomes

$$k(2k + 2l + 1) \sum_{l=0}^{n-1} a_l (2k + l + i)! + E \left( \frac{Z}{\xi} \right)^2 \sum_{l=0}^{n-1} a_l (2k + l + i + 2)! + Z \left( \frac{Z}{\xi} \right)^n \sum_{l=0}^{n-1} a_l (2k + l + i + 1)! = 0. \quad (22)$$

from which we have to determine $E$, $\{a_l\}$, and $\xi$ for a given set of $Z$, $l$, and $n$.

To solve Eq. (22), we introduce a linearly independent basis set defined by

$$(x)_i = \begin{cases} (x + 1)(x + 2)\cdots(x + i) & \text{for } i > 1, \\ 1 & \text{for } i = 0. \end{cases} \quad (23)$$

Then Eq. (22) is rearranged as

$$\left( \frac{Z}{\xi} \right)^2 a_{n-1} (2k + l)_n! + \left( \frac{Z}{\xi} \right)^2 a_{n-2} (2k + l)_{n-1}! + \left( \frac{Z}{\xi} - n \right) a_{n-1} (2k + l)_n + \sum_{i=2}^{n} \left( \frac{Z}{\xi} - i \right) a_{n-i} (2k + l)_{i-1}! - \frac{1}{2} (l + 1) a_l (2k + l)_{i-1} = 0. \quad (24)$$

For Eq. (24) to hold for any non-negative integer $k$, all the coefficients of $\{ (2k + l)_i \}$ must vanish. We immediately have

$$\xi = Z/n, \quad E = -\xi^2/2 = -Z^2/2n^2. \quad (25)$$
and a recursion relation for the expansion coefficients \( \{a_i\} \)

\[
(l - i)(l + i + 1)a_i = 2(n - i)a_{i+1}, \quad i = 1, 2, ..., n - 1,
\]

\[
l(l + 1)a_n = 0. \tag{26a}
\]

When \( n \leq l \), \( l - i \) is positive and therefore Eq. (26a) has a general solution

\[
a_i = \left\{(l + i)(n - i - 1)!(l + i - 1)!(l + i)!\right\}^{-1}a_n. \tag{27a}
\]

Because of Eq. (26b), however, Eq. (27a) trivially results in

\[
a_i = 0, \quad i = 0, 1, ..., n - 1,
\]

and there is no physically meaningful solution for the case of \( n < l \). The well-known quantum condition \( n > l \) or \( l \leq n - 1 \) thus emerges. In this case, Eqs. (26a) and (26b) have a general solution

\[
a_i = \left\{(l - 2)^{(n - l - 1)!(l + i + 1)!/(n - i - 1)!(l + i - 1)!}\right\}^{-1}a_n, \tag{28}
\]

for \( l < i < n - 1 \), for \( 0 < i < n - 1 \).

where \( a_i \) is an arbitrary nonzero constant.

Now the radial function \( R(r) \) [Eq. (21)] becomes

\[
R(r) = \left(\sum_{i=0}^{n-1} a_i \xi_i r^i\right) \exp(-\xi r)
\]

\[
= (\xi r)^i \left(\sum_{i=0}^{n-1} a_i \xi_i r^i\right) \exp(-\xi r), \tag{29a}
\]

where

\[
a_i, i = \left\{\begin{aligned}
(2) & (n - l - 1)!(2l + 1)!
& \times \left\{(n - l - 1)!(l + i + 1)!\right\}^{-1} a_i,
\end{aligned}\right.
\]

\[
\xi = \frac{Z}{\pi n}. \tag{29b}
\]

and \( \xi \) is positive and therefore Eq. (29b) is nothing but the associated Laguerre polynomial \( L_{n+1}^{2l+1}(2\xi r) \). We finally have

\[
R(r) = (\xi r) L_{n+1}^{1} (2\xi r) \exp(-\xi r). \tag{30}
\]

Equations (18), (25), and (30) constitute the complete solutions for the hydrogen-like atom obtained from the present LAPM equation. They are identical to the known results\(^{14} \) which usually follow from the solution of the Schrödinger equation as a second-order differential equation.

B. Ground-state helium atom

The LAPM equation (15) for \( N = 2 \) is

\[
k_1(2k_1 + 1) \left[ r^{2k_1} - 2r^{2k_1} \right] + k_2(2k_2 + 1) \left[ r^{2k_2} - r^{2k_2} \right]
\]

\[
+ E \left[ r^{2k_1} + r^{2k_2} \right] - \left[ r^{2k_1} + r^{2k_2} \right] \Psi(r_1, r_2) = 0, \tag{31}
\]

where

\[
\Psi(r_1, r_2) = - Z/r_1 - Z/r_2 + 1/r_{12}, \tag{32}
\]

for a helium-like atom with nuclear charge \( Z \). Let us consider the approximate wave function given by a single product of the scaled hydrogenic \( 1s \) functions:

\[
\Psi(r_1, r_2) = \exp(-\xi r_1) \exp(-\xi r_2), \tag{33}
\]

which was first examined by Kellner\(^{14} \) in the variational treatment of the ground-state helium atom.

For a special case of \( k_1 = k_2 = 0 \), the explicit evaluation of the integrals appearing in Eq. (31) for the wave function (33) results in a simplified LAPM equation

\[
k_r^2 + 2(k + 1) E
\]

\[
+ \left\{(k + 2)Z - 1 + (k + 3)Z - 2k - 3\right\} \xi = 0, \tag{34}
\]

which includes the quantities \( E \) and \( \xi \) to be determined. In contrast to the case of hydrogen-like atoms, there is no set of \( E \) and \( \xi \) values which satisfies Eq. (34) for all possible \( k \), implying that the exact wave function is not expressed in the form of Eq. (33).

However, we can employ some selected equations from Eq. (34) for an approximate determination of \( E \) and \( \xi \). Let us examine the first two equations resulting from \( k = 0 \) and \( 1 \). They are

\[
E + (Z - 5/16) \xi = 0, \tag{35a}
\]

\[
\xi^2 + 4E + (3Z - \xi) \xi = 0, \tag{35b}
\]

Though we cannot uniquely determine two unknowns from a single equation, Eq. (35a) holds if

\[
\xi = \xi_0 = Z - \xi_0 \quad \text{and} \quad E = E_0 = - \xi_0^2 = (Z - \xi_0)^2, \tag{36a}
\]

which are \( \xi_0 = 1.6875 \) and \( E_0 = -2.847666 \) when \( Z = 2 \). Accidentally, Eq. (36a) is identical to the result of the variational calculation as has been discussed in relation to the zero momentum energy expression.\(^{1} \) Similarly, Eq. (35b) holds if

\[
\xi = \xi_1 = Z - \xi_1 \quad \text{and} \quad E = E_1 = - \xi_1^2 = (Z - \xi_1)^2, \tag{36b}
\]

which become \( \xi_1 = 1.708333 \) and \( E_1 = -2.918403 \) when \( Z = 2 \). This approximate energy \( E_1 \) is lower than the exact energy\(^{15} \) of \( 2.903724 \), since the LAPM energy is not an upper bound to the true energy in general. The unique solutions that satisfy both Eqs. (35a) and (35b) are

\[
\xi = \xi_0 = Z - k \quad \text{and} \quad E = E_0 = -(Z - \xi_0)(Z - \xi_0), \tag{36c}
\]

which become \( \xi_0 = 1.625 \) and \( E_0 = -2.742188 \) for \( Z = 2 \).

In order to clarify the difference in the above three approximate solutions [Eqs. (36a), (36b), and (36c)], it may be convenient to introduce the quantity

\[
\Delta(p_1, p_2) = \left[p_1^2/2 + p_2^2/2 - E\right] \exp(-ir_1p_1 - ir_2p_2)
\]

\[
+ \left[p_1^2 - ir_1p_1 - ir_2p_2\right] V(r_1, r_2). \tag{37}
\]
The condition \( \Delta(p_1, p_2) = 0 \) is equivalent to the Schrödinger equation in momentum space, and hence the deviation of \( \Delta(p_1, p_2) \) from zero characterizes the property of an approximate solution. For a particular case of \( p_2 = 0 \), Eq. (37) reduces to

\[
\delta(p_1) = \Delta(p_1, 0) = (p_1^2/2 - E_0) \left[ \exp(-i r_1 r_0) \right]
\]

\[+ \exp(-i r_1 p_1) V(r_1, r_0) \cdot \cdot \cdot \cdot \cdot \tag{38} \]

For the approximate wave function given by Eq. (33), the difference function \( \delta(p) \) is evaluated to be

\[
\delta(p) = \delta(p) = 32\pi^2 \left( (p^2 - 2E) \right) \left( \xi^{-2} (p^2 + \xi^2)^{-2} \right)
\]

\[+ Z_0 e^{-i(z^2 + \xi^2)^{-1}} \left[ \xi^{-2} (p^2 + \xi^2)^{-1} \right]
\]

\[+ \xi^2 \left[ L_0(p, \xi) E + L_1(p, \xi) E \right], \tag{39} \]

where the explicit forms of the functions \( L_j(p, \xi, E) \) are given in Ref. 16.

In the case of the helium atom \( (Z = 2) \), Fig. 1 shows the \( \delta(p) \) functions for the three sets of approximate parameters, \( (\xi_0, E_0) \), \( (\xi_1, E_1) \), and \( (\xi_2, E_2) \). For the first set obtained from the LAPM equation (34) with \( k = 0 \), the deviation of \( \delta(p) \) from zero is small in the low-momentum region and especially \( \delta(0) = 0 \). For the second set resulting from the LAPM equation with \( k = 1 \), \( | \delta(p) | \) decreases in the high-momentum region, but increases remarkably in the low-momentum region. For the third set, the low-momentum behavior of \( \delta(p) \) is much improved, but a large deviation in the high-momentum region is observed. These behaviors may be easily understood if we are reminded of the fact that the satisfaction of the \( k \) th LAPM equation corresponds to making the coefficient of \( p^{2k} \) zero when \( \delta(p) \) is expanded in a power series of \( p^2 \). In fact, the \( \delta(p) \) functions for the three sets of parameters can be expressed as

\[
\delta_0(p) = 32\pi^2 \left\{ 2(24/31)^2 p^2 \right\} - \left( 37-2/337 \right) p^4 + O(p^6), \tag{40a} \]

\[
\delta_1(p) = 32\pi^2 \left\{ (163/21.3)^2 p^4 \right\} - \left( 79-2^{20.5}/419 \right) p^6 + O(p^8), \tag{40b} \]

\[
\delta_2(p) = 32\pi^2 \left\{ - (21-2^{20}/13)^3 p^8 + O(p^{10}) \right\}. \tag{40c} \]

The low-momentum superiority of the third set [Eq. (36c)] is clear from Eq. (40c). If we adopt a more flexible trial function with several adjustable parameters, we may be able to extend the zero deviation of the \( \delta(p) \) function to the intermediate-momentum region. Such a possibility will be examined in the future.

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