電子分予の動量空間における基底状態の理論的考察

<table>
<thead>
<tr>
<th>著者</th>
<th>高橋敏昭</th>
</tr>
</thead>
<tbody>
<tr>
<td>巻</td>
<td>83</td>
</tr>
<tr>
<td>号</td>
<td>5</td>
</tr>
<tr>
<td>発行年月日</td>
<td>1985-09-01</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10258/938">http://hdl.handle.net/10258/938</a></td>
</tr>
<tr>
<td>doi</td>
<td>info:doi/10.1063/1.449325</td>
</tr>
</tbody>
</table>
One-electron diatomics in momentum space. I. Implication of first iterated solutions for the ground state

Toshikatsu Koga
Department of Applied Chemistry and Department of Applied Science for Energy, Muroran Institute of Technology, Muroran, Hokkaido, 050 Japan

(Received 29 March 1985; accepted 29 May 1985)

For one-electron diatomic systems, an iterative solution of the momentum-space Schrödinger equation is examined using the Fock transformation which enables us to expand the kernel of the integral equation by the four-dimensional spherical harmonics. Starting from the united atom (UA) and simple LCAO approximations, first iterated solutions are derived and their properties are analyzed. The corresponding approximate energy eigenvalues are also obtained as a function of the internuclear distance $R$. The result from the LCAO starting function is found to be reliable semiquantitatively: in the range of $0 < R < 20$, the maximum errors of the ground-state electronic energy are 4.7% and 1.7%, respectively, for the $H_2^+$ and He$H_2^+$ systems, when compared with the exact values.

I. INTRODUCTION

In recent papers,\textsuperscript{1,2} momentum-space perturbation equations for the $H(1s)-H^+$ and $H(1s)-H(1s)$ long-range interactions have been exactly solved in their Schrödinger forms. The approach used there for the solution of integral equations in momentum space consists of two steps: the momentum vector $p$ of an electron is first transformed from the three-dimensional hyperplane onto the four-dimensional hypersphere (Fock transformation).\textsuperscript{3-7} Then the kernel of the integral equation is expanded by the four-dimensional spherical harmonics $\{Y_{n,m}\}$. Due to the orthonormal property of $\{Y_{n,m}\}$, the integral equation is finally reduced to a linear equation which exactly determines the perturbation wave function.

In the present paper, we apply the same method to one-electron diatomic systems such as $H_2^+$ and $HeH_2^+$ in their ground states and examine an iterative solution. The ground-state electronic energy of $H_2^+$ system at a small internuclear distance $R$. We therefore proceed with our study of first iterated solutions in detail. Asymptotic behaviors of the solutions are also examined for small and large internuclear distances. The numerical results for the $H_2^+$ and $HeH_2^+$, together with the analysis of the asymptotic behavior, show that the iterative solution for one-electron diatomics is promising particularly when one adopts the LCAO starting function. Atomic units are used throughout this paper.

II. FOUR-DIMENSIONAL SPHERICAL HARMONICS AND RELATED FUNCTIONS

A. Four-dimensional spherical harmonics $Y_{n,m}(\Omega)$

We project the three-dimensional momentum space onto the four-dimensional sphere centered at the momentum space origin with the radius $p_0$. As we will see later, the value of $p_0$ is directly related to the energy eigenvalue of the system under consideration and is determined at the final stage of the solution. The projective origin is taken at the point $(0,0,0,-p_0)$ in the four-dimensional (Fock) space. Then a momentum vector $p = (p,\theta,\phi)$ in the polar coordinates in the hyperplane is transformed to a point on the hypersphere, which is specified by the three angles $(\alpha,\theta,\phi)$. The two angles $\theta$ and $\phi$ have usual meaning, while the new angle $\alpha (0 < \alpha < \pi)$ represents the radius $p$ ($0 < p < \infty$). The transformation is\textsuperscript{3-7}

$$p = p_0 \tan(\alpha/2), \quad (1a)$$

$$dp = [(p^2 + p_0^2)/2p_0]d\Omega, \quad (1b)$$

$$d\Omega = \sin^2 \alpha \sin \theta \, d\theta \, d\phi, \quad (1c)$$

where $\Omega$ means the collection of the angles $\alpha, \theta, \phi$. In Eq. (1b) and hereafter, we conveniently continue using $p$ to represent $p_0 \tan(\alpha/2)$ even after the Fock transformation is carried out.

In Fock space, we can expand $|p - p'|^{-2}$ (which appears as a kernel of the momentum-space Schrödinger equation) as\textsuperscript{3-5}

$$|p - p'|^{-2} = 4p_0^2 \left[ 4 \sin^2(\alpha/2) (p^2 + p_0^2) (p^2 + p_0^2) \right]^{-1}, \quad (2a)$$
where $\phi$ is the angle spanned between the two points $\Omega$ ($= p$) and $\Omega'$ ($= p'$). $Y_{nlm}(\Omega)$ are four-dimensional spherical harmonics defined by

$$\frac{1}{\sin^2(\phi/2)} - 1 = 2r\ln - 1$$

$$\{ Y_{l}^{m}(fl) \}$$

$$\{ \}$$

$$C_{n,l}(\alpha) = \frac{\sin(n - l - 1)!}{\sin(n + l)!}$$

$$X_{\mu}^{\beta}$$

$$\psi^{(3a)}$$

$$\begin{aligned}
Y^{m}(\Theta) = \left( - i \right)^{l} C_{n,l}(\alpha) Y_{n-l-m}(\Theta) \exp \left( i \phi \right) \\
C_{n,l}(\alpha) = \frac{2n(n - 1)!}{\sin(n + l)!} \frac{\sin \phi}{2}
\end{aligned}$$

$$\begin{aligned}
Y_{nlm}(\Omega) &= (- 1)^{l} C_{n,l}(\alpha) Y_{nlm}(\Omega) \\
Y_{n'l'm'}(\Omega) &= (- 1)^{l'} C_{n',l'}(\alpha) Y_{n'l'm'}(\Omega)
\end{aligned}$$

The momentum-space hydrogenic wave function $\Phi_{nlm}$ is expressed as

$$\begin{aligned}
\Phi_{nlm} \equiv 4p^{2}(\rho^{2} + \rho_{0}^{2})^{-1} Y_{n,l,m}(\Omega),
\end{aligned}$$

where $p_{0}$ plays a role of the exponent $Z/n$, the integers $n$, $l$, $m$ the three quantum numbers.

### B. Functions $S_{n'l'm'}^{nlm}(R)$ and $W_{n'l'm'}^{nlm}(R)$

Let us define a function $S_{n'l'm'}^{nlm}(R)$ by

$$S_{n'l'm'}^{nlm}(R) = \int \exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) \ Y^{m}(\Omega) \ d\Omega. \tag{4}$$

Then we have

$$S_{n'l'm'}^{nlm}(R) \ * = S_{n'l'm'}^{nlm}(- R), \tag{5a}$$

$$S_{n'l'm'}^{nlm}(0) = \delta_{nn'} \delta_{ll'} \delta_{mm'}, \tag{5b}$$

and

$$\begin{aligned}
\exp( - i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} S_{n'l'm'}^{nlm}(R) Y_{n'l'm'}(\Omega), \tag{6a} \\
\exp( - i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} \left[ S_{n'l'm'}^{nlm}(R) \right] \ * Y_{n'l'm'}(\Omega). \tag{6b}
\end{aligned}$$

Using the abbreviation $N = (nlm)$, we find from Eq. (6a) that

$$\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega)$$

can be expanded in two different ways:

$$\begin{aligned}
\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} S_{n'l'm'}^{nlm}(R) Y_{n'l'm'}(\Omega), \\
\exp(- i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} \left[ S_{n'l'm'}^{nlm}(R) \right] \ * Y_{n'l'm'}(\Omega).
\end{aligned}$$

Using the abbreviation $N = (nlm)$, we find from Eq. (6a) that

$$\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega)$$

can be expanded in two different ways:

$$\begin{aligned}
\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} S_{n'l'm'}^{nlm}(R) Y_{n'l'm'}(\Omega), \\
\exp(- i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega) &= \sum_{n'l'm'} \left[ S_{n'l'm'}^{nlm}(R) \right] \ * Y_{n'l'm'}(\Omega).
\end{aligned}$$

Comparison of the right-hand sides of Eq. (7a) gives a sum rule

$$S_{n'l'm'}^{nlm}(R) = \sum_{n'l'm'} S_{n'l'm'}^{nlm}(R) Y_{n'l'm'}(\Omega). \tag{7b}$$

which can be generalized to

$$S_{n'l'm'}^{nlm}(R) = \sum_{n'l'm'} S_{n'l'm'}^{nlm}(R) Y_{n'l'm'}(\Omega). \tag{7b}$$

We therefore find

$$0 < |W_{n'l'm'}^{nlm}(R)| < 1. \tag{11d}$$

The function $W_{n'l'm'}^{nlm}(R)$ can also be shown to have intimate relations with some familiar position-space quantities (see the Appendix).
can determine \( p_0^{(1)} \) and parameters embedded in \( \psi^{(1)}(\Omega) \). \( f \) is therefore governed by the number of unknown parameters. The reference functions \( \{ \chi_i \} \) are chosen by an appropriate physical insight on the system under consideration. Strictly speaking, there remains ambiguity for this choice, but we note that if \( \psi^{(0)}(\Omega) \) is already a correct solution, then the result of Eq. (15) is independent of \( \{ \chi_i \} \).

A. UA approximation

As a starting function \( \psi^{(0)} \), we may assume a hydrogenic 1s function located at the origin of coordinates [see Eqs. (3e) and (13b)],

\[
\psi^{(0)}(\Omega) = Y_{100}(\Omega).
\]

From Eqs. (12c) and (14), the first iterated solution is found to be

\[
\psi^{(1)}(\Omega) = \sum_{n_i m_i} c_{n_i m_i}^{(1)} \left[ \exp(-i p \cdot R_i) Y_{n_i m_i}(\Omega) \right] + c_{n_i m_i}^{(0)} \left[ \exp(-i p \cdot R_i) Y_{n_i m_i}(\Omega) \right],
\]

where

\[
c_{n_i m_i}^{(1)} = \left( Z_a / Z_b \right) S_{n_i m_i}^{(100)}(R_a),
\]

\[
c_{n_i m_i}^{(0)} = \left( Z_b / Z_a \right) S_{n_i m_i}^{(100)}(R_b).
\]

Since \( \left[ \exp(-i p \cdot R_i) Y_{n_i m_i}(\Omega) \right] \) represents a hydrogenic function \( \Phi_{n_i m_i} \) centered at \( R_i \), Eq. (17a) implies:

(i) \( \psi^{(1)} \) is a mixing of an infinite number of hydrogenic functions centered at \( R_a \) and \( R_b \). Namely, the first iterated solution from the UA starting function is an LCAO function. It is interesting to observe that the concept of LCAO emerges in a purely mathematical manner without invoking any physical intuition.

(ii) Mixing coefficients are inversely proportional to the principal quantum number \( n \). The ratio of mixing coefficients of the \((n_i, l, m)\) functions on different centers is

\[
c_{n_i m_i}^{(1)} / c_{n_i m_i}^{(0)} = \left( Z_b / Z_a \right) \left[ S_{n_i m_i}^{(100)}(R_b) / S_{n_i m_i}^{(100)}(R_a) \right],
\]

which shows that this ratio is proportional to that of nuclear charges and is dependent on the coordinate system through the function \( S_{n_i m_i}^{(100)} \).

In the present UA approximation, \( f = 1 \) and hence \( \chi_1(\Omega) = Y_{100}(\Omega) \) seems to be a most natural choice. We then have

\[
p_0^{(1)} = Z_a W_{100}^{(100)}(R_a) + Z_b W_{100}^{(100)}(R_b),
\]

where

\[
W_{100}^{(100)}(R) = \left[ 1 - (1 + t) \exp(-2t) \right] / t, \quad t = p_0^{(1)}|R|,
\]

and \( p_0^{(1)} \) depends on the coordinate system. Note that \( p_0^{(1)} \) also enters into the right-hand side of Eq. (18a).

For a small internuclear separation \( R \), Eq. (18a) can be explicitly solved as a function of \( R \):

\[
p_0^{(1)} = Z_a - (2/3) [Z_a k^2 + Z_b (1 - k^2) Z_a^2 R^2 + (2/3) [Z_a k^3 + Z_b (1 - k^3) Z_a^2 R^3 + O(R^4),
\]

where we have used

\[
\begin{align*}
\langle p^2 / 2 - E \rangle \psi(p) &= (2/3)^{-1} \int |p - p'|^2 \\
&\times \left[ Z_a \exp \left[ -i(p - p') \cdot R_a \right] \right. \\
&\left. + Z_b \exp \left[ -i(p - p') \cdot R_b \right] \right] \psi(p') dp',
\end{align*}
\]

where \( R_a \) and \( R_b \) are position vectors of two nuclei whose charges are \( Z_a \) and \( Z_b \). The nuclear repulsion term has been omitted and \( E \) represents the electronic energy. We discuss only the case of \( E < 0 \) and set

\[
p_0 = \sqrt{-2E}.
\]

We also assume that the momentum wave function is expressed as

\[
\psi(p) = 4p^2 \phi(p) = 4p^2 \phi(\Omega).
\]

Then the Fock transformation [Eqs. (1) and (2)] allows us to rewrite Eq. (12a) as

\[
P(\Omega) \psi(\Omega) = p_0 \phi(\Omega),
\]

where

\[
P(\Omega) \psi(\Omega) = (2\pi^{-1}) \int \left[ 4 \sin^2(\omega/2) \right]^{-1} \\
\times \left[ Z_a \exp \left[ -i(p - p') \cdot R_a \right] \right. \\
+ Z_b \exp \left[ -i(p - p') \cdot R_b \right] \right] \psi(\Omega) d\Omega,
\]

\[
= \sum_{n m} n^{-1} \left[ Z_a \exp \left[ -i(p - p') \cdot R_a \right] \right. \\
\times \left[ \exp(-i p \cdot R_a) Y_{n m}(\Omega) \right] \\
+ Z_b \exp \left[ -i(p - p') \cdot R_b \right] \right] \psi(\Omega) d\Omega,
\]

\[
= \sum_{n m} n^{-1} \left[ Z_a \exp \left[ -i(p - p') \cdot R_a \right] \right. \\
\times \left[ \exp(-i p \cdot R_a) Y_{n m}(\Omega) \right] \\
+ Z_b \exp \left[ -i(p - p') \cdot R_b \right] \right] \psi(\Omega) d\Omega.
\]

The first iterated solution \( \psi^{(1)} \) for the initial guess \( \psi^{(0)} \) (which may include some parameters to be determined) is defined by

\[
\psi^{(1)}(\Omega) = P(\Omega) \psi^{(0)}(\Omega).
\]

In order to obtain approximate eigenvalue \( p_0^{(1)} \) and wave function \( \psi^{(1)}(\Omega) \) at the stage of the first iteration, we introduce a set of reference functions \( \{ \chi_i \} \) (\( i = 1, 2, \ldots, f \)) and consider the \( \chi_i \) component (or the projection onto the \( \chi_i \) axis in the functional space) of \( \psi^{(1)}(\Omega) \) and \( \psi^{(0)}(\Omega) \). From Eq. (12b), we then have

\[
p_0^{(1)} = \int \chi_i^{(1)}(\Omega) \psi^{(1)}(\Omega) d\Omega / \int \chi_i^{(0)}(\Omega) \psi^{(0)}(\Omega) d\Omega, \quad i = 1, 2, \ldots, f.
\]

Equation (15) constitutes a set of equations from which we
we choose $X_1 = \exp(-i \mathbf{p} \cdot \mathbf{R}_a)$, $R = |\mathbf{R}_b - \mathbf{R}_a|$, (19b)

When we employ the center-of-the-charges-of-the-nuclei (CCN) coordinates, $k = Z_u / Z_u$ and we obtain

$$p^{(0)}_0 = Z_u - (2/3)Z_u Z_b R^2 + (2/3)Z_u Z_b Z_r^2 R^2 + (2/3)Z_u Z_b Z_r^2 R^3 + O(R^4),$$

(20a)

$$E^{(1)} = \left[ \frac{p^{(0)}_0}{2} \right]^2 / 2$$

$$= - (1/2)Z_u^2 + (2/3)Z_u Z_b Z_r^2 R^2 - (2/3)Z_u Z_b Z_r^2 R^3 + O(R^4),$$

(20c)

the first iterated energy $E^{(1)}$ is correct up to the order of $R^2$. However, this is not true for coordinate systems other than the CCN one, and the use of the CCN coordinates is suggested for the UA approximation.

On the other hand, we find for a very large $R$ that

$$p^{(0)}_0 \to 0 \text{ and } E^{(1)} \to 0 \text{ as } R \to \infty,$$

(21)

if we use the CCN coordinates. This is obviously incorrect and the results of Eqs. (20b) and (21) mean that the simple UA approximation is valid only for a relatively small internuclear distance.

B. LCAO approximation

We now assume a simple (unnormalized) LCAO function as the starting function,

$$\psi^{(0)}(\mathcal{Q}) = \left[ c_u \exp(-i \mathbf{p} \cdot \mathbf{R}_u) + c_b \exp(-i \mathbf{p} \cdot \mathbf{R}_b) \right] Y_{100}(\mathcal{Q}),$$

(22)

which corresponds to $c_u(1s_u) + c_b(1s_b)$. Since the above LCAO function is the initial and predominant term of the first iterated solution of the UA approximation [see Eq. (17a)], we expect a considerable improvement of the result.

Inserting Eq. (22) into Eq. (14), we obtain the first iterated function

$$\psi^{(1)}(\mathcal{Q}) = \left[ Z_u c_u \exp(-i \mathbf{p} \cdot \mathbf{R}_u) + Z_b c_b \exp(-i \mathbf{p} \cdot \mathbf{R}_b) \right] Y_{100}(\mathcal{Q})$$

$$+ \sum_{n=-1}^{n=1} \left[ Z_u c_b S_{n100}(R) \exp(-i \mathbf{p} \cdot \mathbf{R}_u) + Z_b c_u S_{n100}(R) \exp(-i \mathbf{p} \cdot \mathbf{R}_b) \right] Y_{n}(\mathcal{Q}),$$

(23)

which is again an LCAO function composed of various hydrogenic functions centered at $\mathbf{R}_u$ and $\mathbf{R}_b$.

Since the ratio $c_b / c_u$ is meaningful, $f = 2$ for the present LCAO approximation. For the two reference functions, we choose $X_1 = \exp(-i \mathbf{p} \cdot \mathbf{R}_u) Y_{100}(\mathcal{Q})$ and $X_2 = \exp(-i \mathbf{p} \cdot \mathbf{R}_b) Y_{100}(\mathcal{Q})$ which correspond to (1s), and (1s), respectively. The projections of $\psi^{(0)}$ and $\psi^{(1)}$ onto these reference functions are found to be

\[ (1s)_u \text{ component:} \]

$$\int \chi^{(1)} \psi^{(0)} d\mathcal{Q} = c_u + \left[ S_{100}^{(100)}(R) \right] c_u,$$

(24a)

$$\int \chi^{(1)} \psi^{(1)} d\mathcal{Q} = \left[ Z_u + Z_b W_{100}^{100}(R) \right] c_u + Z_u \left[ S_{100}^{(100)}(R) \right] c_u,$$

(24b)

\[ (1s)_b \text{ component:} \]

$$\int \chi^{(1)} \psi^{(0)} d\mathcal{Q} = \left[ Z_u + Z_b W_{100}^{100}(R) \right] c_u + Z_b,$$

(24c)

$$\int \chi^{(1)} \psi^{(1)} d\mathcal{Q} = Z_u \left[ S_{100}^{(100)}(R) \right] c_u + Z_b \left[ W_{100}^{100}(R) \right] c_u$$

(24d)

$$+ \left[ Z_u + Z_b W_{100}^{100}(R) \right] c_u,$$

where $R = R_b - R_a$, $W_{100}^{100}(R)$ is given in Eq. (18b), and

$$S_{100}^{(100)}(R) = \left[ 1 + t \right] \exp(-t), \quad t = p^{(0)}_0 / |R|,$$

(24e)

From Eq. (15), we then have the following equation for the determination of $p^{(1)}_0$ and $c_u$ and $c_b$:

$$(p^{(1)}_0 - Z_u - Z_b W_{100}^{100}(R)) \left[ S_{100}^{(100)}(R) \right] c_u + Z_u \left[ W_{100}^{100}(R) \right] c_u = (0).$$

(25)

Note that Eq. (25) is linear with respect to $c_u$ and $c_b$ but is nonlinear with respect to $p^{(1)}_0$ because of the functions $W_{100}^{100}$ and $S_{100}^{(100)}$. Different from the UA approximation, $p^{(1)}_0$ is independent of the coordinate system employed.

As in the UA approximation, the explicit solution of Eq. (25) is possible for a small internuclear separation $R$. The results for $p^{(1)}_0$ and $E^{(1)}$ are

$$p^{(1)}_0 = Z_u - (2/3)Z_u Z_b Z_r^2 + (2/3)Z_u Z_b Z_r^2 R^3$$

$$- (2/5)Z_u Z_u \left[ 1 - (5/9)Z_u Z_u / Z_r^2 \right] Z_r^4 R^4 + O(R^5),$$

(26a)

$$E^{(1)} = - (1/2)Z_u^2 + (2/3)Z_u Z_b Z_r^2 R^3 - (2/3)Z_u Z_b Z_r^2 R^3 + (2/5)Z_u Z_u \left[ 1 - (10/9)Z_u Z_u / Z_u^2 \right] Z_r^4 R^4$$

$$+ O(R^5),$$

(26b)

$E^{(1)}$ agrees completely with the correct result [Eq. (20c)] up to the order of $R^3$. The coefficient of $R^4$ in $E^{(1)}$ is partly correct. The asymptotic behavior for a very large $R$ is

$$p^{(1)}_0 \to \left[ Z_u + Z_u - Z_b \right] / 2$$

$$E^{(1)} \to - \left[ Z_u + Z_u - Z_b \right] \right| / 2 \text{ as } R \to \infty,$$

(27)

correctly converges to the atom with larger nuclear charge. As expected, the LCAO approximation has good asymptotic behaviors both at $R \to 0$ and $R \to \infty$, and supports the adequacy of the choice of the reference functions (1s), and (1s),. However, numerical analysis for some specific systems is required to see the validity in the intermediate range of $R$.

C. Numerical results for $H_2^+$ and $HeH^+$

We have calculated the first iterated energy $E^{(1)}$ based on Eq. (18a) (UA approximation with the CCN coordinates)
TABLE I. Negatives of electronic energies (a.u.) for the ground state of the H$_2^+$ system. Values in parentheses are percent errors.

<table>
<thead>
<tr>
<th>R</th>
<th>First iterated</th>
<th>Variational LCAO</th>
<th>Exact$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UA</td>
<td>LCAO</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>2.000 00 (0.0)</td>
<td>2.000 00 (0.0)</td>
<td>2.000 00</td>
</tr>
<tr>
<td>0.1</td>
<td>1976.01 (0.1)</td>
<td>1978.17 (0.0)</td>
<td>1978.21</td>
</tr>
<tr>
<td>0.2</td>
<td>1916.53 (0.6)</td>
<td>1927.99 (0.0)</td>
<td>1928.33</td>
</tr>
<tr>
<td>0.3</td>
<td>1836.76 (1.6)</td>
<td>1864.81 (0.1)</td>
<td>1865.79</td>
</tr>
<tr>
<td>0.4</td>
<td>1748.26 (2.9)</td>
<td>1796.93 (0.2)</td>
<td>1800.75</td>
</tr>
<tr>
<td>0.5</td>
<td>1658.12 (4.4)</td>
<td>1728.67 (0.4)</td>
<td>1731.76</td>
</tr>
<tr>
<td>0.6</td>
<td>1570.36 (6.0)</td>
<td>1662.25 (0.6)</td>
<td>1666.75</td>
</tr>
<tr>
<td>0.8</td>
<td>1409.08 (9.4)</td>
<td>1538.72 (1.0)</td>
<td>1546.57</td>
</tr>
<tr>
<td>1.0</td>
<td>1269.82 (12.5)</td>
<td>1429.34 (1.5)</td>
<td>1441.00</td>
</tr>
<tr>
<td>1.5</td>
<td>1005.40 (19.5)</td>
<td>1212.84 (2.9)</td>
<td>1233.79</td>
</tr>
<tr>
<td>2.0</td>
<td>0824.98 (25.2)</td>
<td>1059.18 (3.9)</td>
<td>1086.51</td>
</tr>
<tr>
<td>2.5</td>
<td>0696.40 (29.9)</td>
<td>0948.69 (4.5)</td>
<td>0978.76</td>
</tr>
<tr>
<td>3.0</td>
<td>0600.91 (34.0)</td>
<td>0867.87 (4.7)</td>
<td>0897.78</td>
</tr>
<tr>
<td>4.0</td>
<td>0469.55 (41.0)</td>
<td>0762.50 (4.2)</td>
<td>0787.33</td>
</tr>
<tr>
<td>5.0</td>
<td>0384.05 (47.0)</td>
<td>0701.00 (3.2)</td>
<td>0719.21</td>
</tr>
<tr>
<td>6.0</td>
<td>0324.26 (52.2)</td>
<td>0662.34 (2.3)</td>
<td>0675.75</td>
</tr>
<tr>
<td>8.0</td>
<td>0246.54 (60.7)</td>
<td>0619.89 (1.2)</td>
<td>0626.73</td>
</tr>
<tr>
<td>10.0</td>
<td>0198.48 (67.0)</td>
<td>0590.00 (0.8)</td>
<td>0600.30</td>
</tr>
<tr>
<td>15.0</td>
<td>0133.05 (76.5)</td>
<td>0564.70 (0.4)</td>
<td>0566.67</td>
</tr>
<tr>
<td>20.0</td>
<td>0099.93 (81.8)</td>
<td>0548.86 (0.2)</td>
<td>0550.00</td>
</tr>
</tbody>
</table>

$^a$References 11 and 12.

and Eq. (25) (LCAO approximation), and compared the results with the corresponding variational LCAO and exact values for a wide range of $R$. The results are summarized in Tables I and II for the H$_2^+$ and HeH$_2^+$ systems, respectively.

In both systems, the general feature of the UA and LCAO approximations is consistent with the analysis given in the previous subsections. The UA approximation is valid only for very small values of $R$. The error increases monotonically as $R$ increases. On the other hand, the results of the LCAO approximation are acceptable not only for the small and large $R$ regions but also for the intermediate region. The maximum errors relative to the exact values are found to be 4.7% at $R = 3.0$ (H$_2^+$) and 1.7% at $R = 1.0$–1.5 (HeH$_2^+$). The LCAO approximation is reliable semiquantitatively, and the iterative solution with this method seems to be promising.

When compared with the corresponding variational LCAO calculation, however, the error of the first iterated LCAO is about three times larger in the intermediate $R$ region, and the first iterated LCAO solution is still open to further improvement. Second and more iterations are possible methods for this purpose. Another direction of improvement is the use of an extended LCAO starting function which includes some additional AO's such as $2p\sigma$ AO.

However, the primary merit of the momentum space approach will not be to obtain accurate numerical values, since the usual variational method and its sophisticated version in position space are obviously more direct and powerful for this purpose as long as the problem of electronic structures of atoms and molecules is concerned. Rather, the momentum space approach can be regarded as a hopeful tool which permits us to explore new (or complementary, at least) concepts and pictures that are "hidden" in the ordinary position space but useful to grope for a new development in the electronic structure theory. Nonvariational calculation and the resultant analysis of short-range interactions, presented in this study, may be located along this line, in which we have seen that fewer kinds of integrals are sufficient than those required in the variational calculations.

ACKNOWLEDGMENT

Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

APPENDIX

The following position-space interpretation is possible for the functions $S_{\omega,\nu}^{\text{lim}}(R)$ and $W_{\omega,\nu}^{\text{lim}}(R)$ introduced in Sec. II.

Let $u_{\omega,\nu}(r)$ be the hydrogenic wave function in position space. Then the following correspondence holds through the Fourier transformation (FT):

$$u_{\omega,\nu}(r - R) \propto \exp(-\mu R) \delta_{\omega,\nu}(p),$$

$$r^{-1} u_{\omega,\nu}(r) r^{-1} = \int |p - p'|^{-2} \delta_{\omega,\nu}(p') dp' = [2p_0^2/(p^2 + p_0^2)] Y_{\omega,\nu}(\Omega).$$

Therefore we obtain

$$\int u_{\omega,\nu}^{\ast}(r - R) |r|^{-1} u_{\omega,\nu}(r) dr = \int [\exp(-\mu R) \delta_{\omega,\nu}(p)^*] \times [2p_0^2/(p^2 + p_0^2)] Y_{\omega,\nu}(\Omega) dp$$

References 13 and 14.
Toshikatsu Koga: One-electron diatomics in momentum space.

\[ p_0 \int \exp(-i\mathbf{p} \cdot \mathbf{R}) Y_{n\ell m}^*(\Omega) Y_{n\ell m}(\Omega) d\Omega \]

\[ = p_0 S_{n\ell m}^{(\text{lim})}(\mathbf{R}), \]  \hspace{1cm} (A3)

which implies that the function \( S_{n\ell m}^{(\text{lim})}(\mathbf{R}) \) is proportional to the nuclear attraction integral in position space over the hydrogenic functions. As a result,

\[ S_{n\ell m}^{(\text{lim})}(\mathbf{R}) \rightarrow 0 \quad \text{as} \quad |\mathbf{R}| \rightarrow \infty. \]  \hspace{1cm} (A4)

Alternative correspondence was given by Shibuya and Wulfman (see also Refs. 5 and 9). The result is

\[ S_{n\ell m}^{(\text{lim})}(\mathbf{R}) = \frac{1}{2\pi} \sum_{\nu, \mu} (2\pi^2 p_0)^{1/2} Y_{n\ell m}^{(\text{lim})} Y_{\nu\mu} \Psi_{\nu\mu}(\mathbf{R}), \]  \hspace{1cm} (A5)

\[ Y_{n\ell m}^{(\text{lim})} = \left( \frac{2\pi^2}{p_0} \right)^{1/2} \left[ 2 Y_{100}(\Omega) + Y_{200}(\Omega) \right] Y_{n\ell m}(\Omega) \]

\[ \times Y_{\nu\mu}^{*}(\Omega) Y_{\nu\mu}(\Omega) d\Omega, \]  \hspace{1cm} (A6)

and \( S_{n\ell m}^{(\text{lim})}(\mathbf{R}) \) is expressible by a linear combination of a finite number of position-space hydrogenic functions.

Similarly, considering another correspondence

\[ |\mathbf{r} - \mathbf{R}|^{-1} u_{n\ell m}(r) \approx (2\pi)^{-1} \int |\mathbf{p} - \mathbf{p}'|^{-2} \exp[-i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{R}] \]

\[ \cdot \Phi_{n\ell m}(\mathbf{p}') d\mathbf{p}' \]

\[ = \left[ 2 p_0^{3/2}/(p^2 + p_0^2) \right] \exp(-i\mathbf{p} \cdot \mathbf{R}) \]

\[ \times \sum_{\nu, \mu} Y_{n\ell m}^{(\text{lim})}(\mathbf{R}) Y_{\nu\mu}(\Omega), \]  \hspace{1cm} (A7)

we have

\[ \int u_{n\ell m}^*(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} u_{n\ell m}(\mathbf{r}) d\mathbf{r} \]

\[ = p_0 \int \sum_{\nu, \mu} Y_{n\ell m}^{(\text{lim})}(\mathbf{R}) Y_{\nu\mu}(\Omega) \]

\[ \times \left[ \exp(-i\mathbf{p} \cdot \mathbf{R}) Y_{n\ell m}^{*}(\Omega) \right] d\mathbf{r} \]

\[ = p_0 W_{n\ell m}^{(\text{lim})}(\mathbf{R}), \]  \hspace{1cm} (A8)

Thus the function \( W_{n\ell m}^{(\text{lim})}(\mathbf{R}) \) is proportional to another kind of nuclear attraction integral in position space, and

\[ W_{n\ell m}^{(\text{lim})}(\mathbf{R}) \rightarrow 0 \quad \text{as} \quad |\mathbf{R}| \rightarrow \infty. \]  \hspace{1cm} (A9)

We note that in the above equations, the exponents of \( u_{n\ell m}(\mathbf{r}) \) should be taken to be \( p_0 \).