One-electron diatomics in momentum space. I. Implication of first iterated solutions for the ground state

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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 $0 \leqslant R \leqslant 20$, the maximum errors of the ground-state electronic energy are 4.7% and 1.7%, respectively, for the H_2^+ and HeH^{2+} systems, when compared with the exact values.

I. INTRODUCTION

In recent papers,[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 $\mathbf{p}$ of an electron is first transformed from the three-dimensional hyperplane onto the four-dimensional hypersphere (Fock transformation).[3–7] Then the kernel of the integral equation is expanded by the four-dimensional spherical harmonics $\{Y_{nlm}\}$. Due to the orthonormal property of $\{Y_{nlm}\}$, 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 momentum-space solution of the H_2^+ molecule was first investigated by McWeeny.[8] He concluded that the iterative method is not very convenient because the required integrations are quite complicated. Introducing the method of Fock transformation, however, Shibuya and Wulfman[4] showed that these integrations are possible even when one starts from the LCAO approximation for the iteration, and estimated the ground-state electronic energy of H_2^+ system at a small internuclear distance R. We therefore proceed with our study along the line developed by Shibuya and Wulfman, but we devise a new method to determine approximate wave functions and eigenvalues for a wide range of R. We also analyze the property of first iterated solutions in detail, which was not given in the work of Shibuya and Wulfman. In the next section, we outline the Fock transformation and define the four-dimensional spherical harmonics $\{Y_{nlm}\}$. In addition, two functions $S^{nlm}_{n'l'm'}(\mathbf{R})$ and $W^{nlm}_{n'l'm'}(\mathbf{R})$ are discussed, which are useful for the many-center problem in Fock space. Though these functions were originally introduced by Shibuya and Wulfman,[4] we here clarify various important properties and relations. In Sec. III, first iterated solutions are derived starting from the united atom (UA) and LCAO wave functions and their implication is discussed. 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 $Y_{nlm}(\Omega)$

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 $\mathbf{p}$ [$=(p,\theta,\phi)$ in the polar coordinates] in the hyperplane is transformed to a point on the hypersphere, which is specified by the three angles (α,θ,ϕ). The two angles θ and ϕ have usual meaning, while the new angle α $(0 \leqslant \alpha < \pi)$ represents the radius p $(0 \leqslant p < \infty)$. The transformation is[3–7]

$$p = p_0 \tan(\alpha/2), \tag{1a}$$

$$d\mathbf{p} = [(p^2 + p_0^2)/2p_0]^3 d\Omega, \tag{1b}$$

$$d\Omega = \sin^2\alpha \sin\theta \, d\alpha \, d\theta \, d\phi, \tag{1c}$$

where Ω means the collection of the angles α, θ, and ϕ. 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 $|\mathbf{p} - \mathbf{p}'|^{-2}$ (which appears as a kernel of the momentum-space Schrödinger equation) as[3–5]

$$|\mathbf{p} - \mathbf{p}'|^{-2} = 4p_0^2 [4 \sin^2(\omega/2)(p^2 + p_0^2)(p'^2 + p_0^2)]^{-1}, \tag{2a}$$

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$$[4\sin^2(\omega/2)]^{-1} = 2\pi^2 \sum_{nlm} n^{-1} Y^*_{nlm}(\Omega')Y_{nlm}(\Omega), \tag{2b}$$

where ω is the angle spanned between the two points Ω ($=\mathbf{p}$) and Ω' ($=\mathbf{p}'$). $\{Y_{nlm}(\Omega)\}$ are four-dimensional spherical harmonics defined by[5]

$$Y_{nlm}(\Omega) = (-i)^l C_{n,l}(\alpha) Y_{lm}(\theta,\phi), \tag{3a}$$

$$C_{n,l}(\alpha) = \{2n(n-l-1)!/[\pi(n+l)!]\}^{1/2} \sin^l\alpha \times [d^{\,l} C^{\,1}_{n-1}(\mu)/d\mu^l]_{\mu=\cos\alpha}, \tag{3b}$$

where $\{Y_{lm}(\theta,\phi)\}$ are usual three-dimensional spherical harmonics and $C^{\nu}_{n}(\mu)$ denotes the Gegenbauer polynomial. The $\{Y_{nlm}\}$ satisfy

$$\int Y^*_{nlm}(\Omega) Y_{n'l'm'}(\Omega) d\Omega = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{3c}$$

$$Y^*_{nlm}(\Omega) = (-1)^{l-m} Y_{nl-m}(\Omega). \tag{3d}$$

The momentum-space hydrogenic wave function Φ_{nlm} is expressed as

$$\Phi_{nlm} = 4p_0^{5/2}(p^2+p_0^2)^{-2} Y_{nlm}(\Omega), \tag{3e}$$

where p_0 plays a role of the exponent Z/n, and the integers n, l, m the three quantum numbers.

B. Functions $S^{nlm}_{n'l'm'}(\mathbf{R})$ and $W^{nlm}_{n'l'm'}(\mathbf{R})$

Let us define a function $S^{nlm}_{n'l'm'}(\mathbf{R})$ by

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

Then we see[4]

$$[S^{nlm}_{n'l'm'}(\mathbf{R})]^* = S^{n'l'm'}_{nlm}(-\mathbf{R}), \tag{5a}$$

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

and

$$\exp(+i\mathbf{p}\cdot\mathbf{R}) Y_{nlm}(\Omega) = \sum_{n'l'm'} S^{nlm}_{n'l'm'}(\mathbf{R}) Y_{n'l'm'}(\Omega), \tag{6a}$$

$$\exp(-i\mathbf{p}\cdot\mathbf{R}) Y_{nlm}(\Omega) = \sum_{n'l'm'} [S^{n'l'm'}_{nlm}(\mathbf{R})]^* Y_{n'l'm'}(\Omega). \tag{6b}$$

Using the abbreviation $N=(nlm)$, we find from Eq. (6a) that $\exp[i\mathbf{p}\cdot(\mathbf{R}_1+\mathbf{R}_2)] Y_{nlm}(\Omega)$ can be expanded in two different ways:

$$\exp[i\mathbf{p}\cdot(\mathbf{R}_1+\mathbf{R}_2)] Y_N(\Omega) = \begin{cases} \sum_{N'} S^N_{N'}(\mathbf{R}_1+\mathbf{R}_2) Y_{N'}(\Omega), \\ \sum_{N'}\sum_{N''} S^N_{N'}(\mathbf{R}_1) S^{N'}_{N''}(\mathbf{R}_2) Y_{N''}(\Omega). \end{cases} \tag{7a}$$

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

$$S^N_{N'}(\mathbf{R}_1+\mathbf{R}_2) = \sum_{N''} S^N_{N''}(\mathbf{R}_1) S^{N''}_{N'}(\mathbf{R}_2) = \sum_{N''} S^{N''}_{N'}(\mathbf{R}_1) S^N_{N''}(\mathbf{R}_2), \tag{7b}$$

which can be generalized to

$$S^N_{N_j}(\mathbf{R}_1+\cdots+\mathbf{R}_j) = \sum_{N_1}\cdots\sum_{N_{j-1}} S^N_{N_1}(\mathbf{R}_1) S^{N_1}_{N_2}(\mathbf{R}_2)\cdots S^{N_{j-1}}_{N_j}(\mathbf{R}_j), \tag{7c}$$

if we consider different expansions of $\exp[i\mathbf{p}\cdot(\mathbf{R}_1+\cdots+\mathbf{R}_j)] Y_N(\Omega)$.

Integrating the product of Eq. (6a) and its complex conjugate over Ω, we have

$$\sum_{\nu\lambda\mu} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) [S^{n'l'm'}_{\nu\lambda\mu}(\mathbf{R})]^* = \delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{8a}$$

and especially for $(nlm)=(n'l'm')$,

$$\sum_{n'l'm'} |S^{nlm}_{n'l'm'}(\mathbf{R})|^2 = 1, \tag{8b}$$

from which it follows that

$$0 \leqslant |S^{nlm}_{n'l'm'}(\mathbf{R})| \leqslant 1. \tag{8c}$$

A position-space picture of the function $S^{nlm}_{n'l'm'}(\mathbf{R})$ is given in the Appendix.

We next define a function $W^{nlm}_{n'l'm'}(\mathbf{R})$ as

$$W^{nlm}_{n'l'm'}(\mathbf{R}) = \sum_{\nu\lambda\mu} \nu^{-1} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) \int Y_{\nu\lambda\mu}(\Omega) \times [\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega)]^* d\Omega = \sum_{\nu\lambda\mu} \nu^{-1} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) [S^{n'l'm'}_{\nu\lambda\mu}(\mathbf{R})]^*. \tag{9}$$

Then the following relations hold:

$$[W^{nlm}_{n'l'm'}(\mathbf{R})]^* = W^{n'l'm'}_{nlm}(\mathbf{R}), \tag{10a}$$

$$W^{nlm}_{n'l'm'}(\mathbf{0}) = n^{-1}\delta_{nn'}\delta_{ll'}\delta_{mm'}, \tag{10b}$$

$$\sum_{n'l'm'} n'^{-1} S^{nlm}_{n'l'm'}(\mathbf{R}) Y_{n'l'm'}(\Omega) = \sum_{n'l'm'} W^{nlm}_{n'l'm'}(\mathbf{R}) [\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega)]. \tag{10c}$$

Similar to the function $S^{nlm}_{n'l'm'}(\mathbf{R})$, we can derive several sum rules for $W^{nlm}_{n'l'm'}(\mathbf{R})$. For example,

$$\sum_{n'l'm'} W^{nlm}_{n'l'm'}(\mathbf{R}) S^{n'l'm'}_{nlm}(\mathbf{R}) = n^{-1} S^{nlm}_{nlm}(\mathbf{R}), \tag{11a}$$

$$\sum_{\nu\lambda\mu} \nu^{-2} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) [S^{n'l'm'}_{\nu\lambda\mu}(\mathbf{R})]^* = \sum_{\nu\lambda\mu} W^{nlm}_{\nu\lambda\mu}(\mathbf{R}) [W^{n'l'm'}_{\nu\lambda\mu}(\mathbf{R})]^*, \tag{11b}$$

and a special case of Eq. (11b) for $(nlm)=(n'l'm')$ is

$$\sum_{n'l'm'} |W^{nlm}_{n'l'm'}(\mathbf{R})|^2 = \sum_{n'l'm'} n'^{-2} |S^{nlm}_{n'l'm'}(\mathbf{R})|^2 \leqslant \sum_{n'l'm'} |S^{nlm}_{n'l'm'}(\mathbf{R})|^2 = 1. \tag{11c}$$

We therefore find

$$0 \leqslant |W^{nlm}_{n'l'm'}(\mathbf{R})| \leqslant 1. \tag{11d}$$

The function $W^{nlm}_{n'l'm'}(\mathbf{R})$ can also be shown to have intimate relations with some familiar position-space quantities (see the Appendix).

III. FIRST ITERATED SOLUTIONS

The momentum-space Schrödinger equation for a one-electron diatomic system is given by[4,5,8,9]

$$(p^2/2-E)\Psi(\mathbf{p})=(2\pi^2)^{-1}\int|\mathbf{p}-\mathbf{p}'|^{-2}\times\{Z_a\exp[-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_a]+Z_b\exp[-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_b]\}\Psi(\mathbf{p}')d\mathbf{p}', \tag{12a}$$

where $\mathbf{R}_a$ and $\mathbf{R}_b$ 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 $E\leqslant 0$ and set

$$p_0=\sqrt{-2E}. \tag{13a}$$

We also assume that the momentum wave function is expressed as

$$\Psi(\mathbf{p})=4p_0^{5/2}(p^2+p_0^2)^{-2}\psi(\Omega). \tag{13b}$$

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

$$P(\Omega)\psi(\Omega)=p_0\psi(\Omega), \tag{12b}$$

where

$$\begin{aligned}P(\Omega)\psi(\Omega)&=(2\pi^2)^{-1}\int[4\sin^2(\omega/2)]^{-1}\times\{Z_a\exp[-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_a]+Z_b\exp[-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_b]\}\psi(\Omega')d\Omega'\\&=\sum_{nlm}n^{-1}\Big\{Z_a\exp(-i\mathbf{p}\cdot\mathbf{R}_a)Y_{nlm}(\Omega)\times\int[\exp(-i\mathbf{p}'\cdot\mathbf{R}_a)Y_{nlm}(\Omega')]^*\psi(\Omega')d\Omega'\\&\quad+Z_b\exp(-i\mathbf{p}\cdot\mathbf{R}_b)Y_{nlm}(\Omega)\times\int[\exp(-i\mathbf{p}'\cdot\mathbf{R}_b)Y_{nlm}(\Omega')]^*\psi(\Omega')d\Omega'\Big\}.\end{aligned} \tag{12c}$$

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

$$\psi^{(1)}(\Omega)=P(\Omega)\psi^{(0)}(\Omega). \tag{14}$$

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 χ_i component (or the projection onto the χ_i axis in the functional space) of $\psi^{(0)}(\Omega)$ and $\psi^{(1)}(\Omega)$. From Eq. (12b), we then have

$$p_0^{(1)}=\int\chi_i^*(\Omega)\psi^{(1)}(\Omega)d\Omega\Big/\int\chi_i^*(\Omega)\psi^{(0)}(\Omega)d\Omega,\quad i=1,2,\ldots,f. \tag{15}$$

Equation (15) constitutes a set of equations from which we 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)],

$$\psi^{(0)}(\Omega)=Y_{100}(\Omega). \tag{16}$$

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

$$\psi^{(1)}(\Omega)=\sum_{nlm}\{c_{nlm}^a[\exp(-i\mathbf{p}\cdot\mathbf{R}_a)Y_{nlm}(\Omega)]+c_{nlm}^b[\exp(-i\mathbf{p}\cdot\mathbf{R}_b)Y_{nlm}(\Omega)]\}, \tag{17a}$$

where

$$\begin{aligned}c_{nlm}^a&=(Z_a/n)S_{nlm}^{100}(\mathbf{R}_a),\\c_{nlm}^b&=(Z_b/n)S_{nlm}^{100}(\mathbf{R}_b).\end{aligned} \tag{17b}$$

Since $[\exp(-i\mathbf{p}\cdot\mathbf{R}_a)Y_{nlm}(\Omega)]$ represents a hydrogenic function Φ_{nlm} centered at $\mathbf{R}_a$, Eq. (17a) implies:

(i) $\psi^{(1)}$ is a mixing of an infinite number of hydrogenic functions centered at $\mathbf{R}_a$ and $\mathbf{R}_b$. 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,l,m) functions on different centers is

$$c_{nlm}^b/c_{nlm}^a=(Z_b/Z_a)[S_{nlm}^{100}(\mathbf{R}_b)/S_{nlm}^{100}(\mathbf{R}_a)], \tag{17c}$$

which shows that this ratio is proportional to that of nuclear charges and is dependent on the coordinate system through the function S_{nlm}^{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

$$p_0^{(1)}=Z_a W_{100}^{100}(\mathbf{R}_a)+Z_b W_{100}^{100}(\mathbf{R}_b), \tag{18a}$$

where

$$W_{100}^{100}(\mathbf{R})=[1-(1+t)\exp(-2t)]/t,\quad t=p_0^{(1)}|\mathbf{R}|, \tag{18b}$$

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:

$$p_0^{(1)}=Z_u-(2/3)[Z_a k^2+Z_b(1-k)^2]Z_u^2R^2+(2/3)[Z_a k^3+Z_b(1-k)^3]Z_u^3R^3+O(R^4), \tag{19a}$$

where we have used

$$Z_u = Z_a + Z_b, \quad R = |\mathbf{R}_b - \mathbf{R}_a|, \tag{19b}$$

$$R_a = |\mathbf{R}_a| = kR, \quad R_b = |\mathbf{R}_b| = (1-k)R.$$

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

$$p_0^{(1)} = Z_u - (2/3)Z_aZ_bZ_uR^2 + (2/3)Z_aZ_b(Z_a^2 + Z_b^2)R^3 + O(R^4), \tag{20a}$$

$$E^{(1)} = -[p_0^{(1)}]^2/2 = -(1/2)Z_u^2 + (2/3)Z_aZ_bZ_u^2R^2 - (2/3)Z_aZ_bZ_u(Z_a^2 + Z_b^2)R^3 + O(R^4). \tag{20b}$$

Since the correct short-range behavior is known to be[10]

$$E = -(1/2)Z_u^2 + (2/3)Z_aZ_bZ_uR^2 - (2/3)Z_aZ_bZ_u^3R^3 + (2/5)Z_aZ_b[1 - (64/27)(Z_aZ_b/Z_u^2)]Z_u^4R^4 + O(R^5), \tag{20c}$$

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

$$p_0^{(1)} \to 0 \text{ and } E^{(1)} \to 0 \text{ as } R \to \infty, \tag{21}$$

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,

$$\psi^{(0)}(\Omega) = [c_a \exp(-i\mathbf{p}\cdot\mathbf{R}_a) + c_b \exp(-i\mathbf{p}\cdot\mathbf{R}_b)]\, Y_{100}(\Omega), \tag{22}$$

which corresponds to $c_a(1s)_a + c_b(1s)_b$. 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

$$\psi^{(1)}(\Omega) = [Z_ac_a \exp(-i\mathbf{p}\cdot\mathbf{R}_a) + Z_bc_b \exp(-i\mathbf{p}\cdot\mathbf{R}_b)]\, Y_{100}(\Omega) + \sum_{nlm} n^{-1}[Z_ac_bS_{nlm}^{100}(-\mathbf{R})\exp(-i\mathbf{p}\cdot\mathbf{R}_a) + Z_bc_aS_{nlm}^{100}(\mathbf{R})\exp(-i\mathbf{p}\cdot\mathbf{R}_b)]\, Y_{nlm}(\Omega), \tag{23}$$

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

Since the ratio c_b/c_a is meaningful, $f = 2$ for the present LCAO approximation. For the two reference functions, we choose $\chi_1 = \exp(-i\mathbf{p}\cdot\mathbf{R}_a)Y_{100}(\Omega)$ and $\chi_2 = \exp(-i\mathbf{p}\cdot\mathbf{R}_b)Y_{100}(\Omega)$ which correspond to $(1s)_a$ and $(1s)_b$, respectively. The projections of $\psi^{(0)}$ and $\psi^{(1)}$ onto these reference functions are found to be

$(1s)_a$ component:

$$\int \chi_1^* \psi^{(0)} d\Omega = c_a + [S_{100}^{100}(\mathbf{R})]^* c_b, \tag{24a}$$

$$\int \chi_1^* \psi^{(1)} d\Omega = [Z_a + Z_bW_{100}^{100}(\mathbf{R})]c_a + Z_u[S_{100}^{100}(\mathbf{R})]^* c_b, \tag{24b}$$

$(1s)_b$ component:

$$\int \chi_2^* \psi^{(0)} d\Omega = [S_{100}^{100}(\mathbf{R})]c_a + c_b, \tag{24c}$$

$$\int \chi_2^* \psi^{(1)} d\Omega = Z_u[S_{100}^{100}(\mathbf{R})]c_a + \{Z_a[W_{100}^{100}(\mathbf{R})]^* + Z_b\}c_b, \tag{24d}$$

where $\mathbf{R} = \mathbf{R}_b - \mathbf{R}_a$, $W_{100}^{100}(\mathbf{R})$ is given in Eq. (18b), and

$$S_{100}^{100}(\mathbf{R}) = (1+t)\exp(-t), \quad t = p_0^{(1)}|\mathbf{R}|. \tag{24e}$$

From Eq. (15), we then have the following equation for the determination of $p_0^{(1)}$ and c_b/c_a:

$$\begin{pmatrix} p_0^{(1)} - Z_a - Z_bW_{100}^{100} & (p_0^{(1)} - Z_u)[S_{100}^{100}]^* \\ (p_0^{(1)} - Z_u)S_{100}^{100} & p_0^{(1)} - Z_a[W_{100}^{100}]^* - Z_b \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{25}$$

Note that Eq. (25) is linear with respect to c_a and c_b but is nonlinear with respect to $p_0^{(1)}$ because of the functions W_{100}^{100} and S_{100}^{100}. Different from the UA approximation, $p_0^{(1)}$ 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 $p_0^{(1)}$ and $E^{(1)}$ are

$$p_0^{(1)} = Z_u - (2/3)Z_aZ_bZ_uR^2 + (2/3)Z_aZ_bZ_u^2R^3 - (2/5)Z_aZ_b[1 - (5/9)Z_aZ_b/Z_u^2]Z_u^3R^4 + O(R^5), \tag{26a}$$

$$E^{(1)} = -(1/2)Z_u^2 + (2/3)Z_aZ_bZ_u^2R^2 - (2/3)Z_aZ_bZ_u^3R^3 + (2/5)Z_aZ_b[1 - (10/9)Z_aZ_b/Z_u^2]Z_u^4R^4 + O(R^5). \tag{26b}$$

$E^{(1)}$ 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

$$\left.\begin{aligned} p_0^{(1)} &\to [Z_u + |Z_a - Z_b|]/2 \\ E^{(1)} &\to -[Z_u + |Z_a - Z_b|]^2/8 \end{aligned}\right\} \text{as } R \to \infty, \tag{27}$$

and 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 $(1s)_a$ and $(1s)_b$. 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^{2+}

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.

R	First iterated		Variational	Exact[a]
	UA	LCAO	LCAO	
0.0	2.000 00 (0.0)	2.000 00 (0.0)	2.000 00 (0.0)	2.000 00
0.1	1.976 19 (0.1)	1.978 17 (0.0)	1.978 21 (0.0)	1.978 24
0.2	1.916 53 (0.6)	1.927 99 (0.0)	1.928 33 (0.0)	1.928 62
0.3	1.836 76 (1.6)	1.864 81 (0.1)	1.865 79 (0.0)	1.866 70
0.4	1.748 26 (2.9)	1.796 93 (0.2)	1.798 84 (0.1)	1.800 75
0.5	1.658 12 (4.4)	1.728 67 (0.4)	1.731 76 (0.2)	1.734 99
0.6	1.570 36 (6.0)	1.662 25 (0.6)	1.666 75 (0.3)	1.671 48
0.8	1.409 08 (9.4)	1.538 72 (1.0)	1.546 57 (0.5)	1.554 48
1.0	1.269 82 (12.5)	1.429 34 (1.5)	1.441 00 (0.7)	1.451 79
1.5	1.005 40 (19.5)	1.212 84 (2.9)	1.233 79 (1.2)	1.248 99
2.0	0.824 98 (25.2)	1.059 18 (3.9)	1.086 51 (1.5)	1.102 63
2.5	0.696 40 (29.9)	0.948 69 (4.5)	0.978 76 (1.5)	0.993 82
3.0	0.600 91 (34.0)	0.867 87 (4.7)	0.897 78 (1.4)	0.910 90
4.0	0.469 55 (41.0)	0.762 50 (4.2)	0.787 33 (1.1)	0.796 08
5.0	0.384 05 (47.0)	0.701 00 (3.2)	0.719 21 (0.7)	0.724 42
6.0	0.324 26 (52.2)	0.662 92 (2.3)	0.675 75 (0.4)	0.678 64
8.0	0.246 54 (60.7)	0.619 89 (1.2)	0.626 73 (0.1)	0.627 57
10.0	0.198 48 (67.0)	0.596 00 (0.8)	0.600 30 (0.0)	0.600 58
15.0	0.133 05 (76.5)	0.564 70 (0.4)	0.566 67 (0.0)	0.566 72
20.0	0.099 93 (81.8)	0.548 86 (0.2)	0.550 00 (0.0)	0.550 01

[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.

TABLE II. Negatives of electronic energies (a.u.) for the ground state of the HeH^{2+} system. Values in parentheses are percent errors.

R	First iterated		Variational	Exact[a]
	UA	LCAO	LCAO	
0.0	4.500 00 (0.0)	4.500 00 (0.0)	4.500 00 (0.0)	4.500 00
0.1	4.400 64 (0.2)	4.410 83 (0.0)	4.411 10 (0.0)	4.411 32
0.2	4.177 92 (1.3)	4.229 34 (0.1)	4.231 07 (0.0)	4.232 70
0.3	3.912 89 (3.0)	4.025 32 (0.2)	4.029 67 (0.1)	4.034 14
0.4	3.646 78 (5.1)	3.826 02 (0.4)	3.833 88 (0.2)	3.842 06
0.5	3.396 90 (7.3)	3.641 53 (0.7)	3.653 54 (0.3)	3.665 55
0.6	3.168 99 (9.6)	3.475 04 (0.9)	3.491 53 (0.4)	3.506 89
0.8	2.779 46 (14.2)	3.196 26 (1.4)	3.221 27 (0.6)	3.240 84
1.0	2.465 84 (18.7)	2.981 94 (1.7)	3.012 96 (0.7)	3.033 36
1.5	1.910 34 (29.1)	2.648 94 (1.7)	2.680 88 (0.5)	2.695 46
2.0	1.552 24 (38.2)	2.480 64 (1.3)	2.504 35 (0.3)	2.512 20
2.5	1.304 15 (45.8)	2.384 41 (0.9)	2.401 00 (0.2)	2.404 89
3.0	1.122 74 (51.9)	2.321 59 (0.6)	2.333 54 (0.1)	2.335 49
4.0	0.875 98 (61.1)	2.243 04 (0.3)	2.250 01 (0.0)	2.250 61
5.0	0.716 51 (67.4)	2.195 45 (0.2)	2.200 00 (0.0)	2.200 24
6.0	0.605 27 (72.1)	2.163 46 (0.2)	2.166 67 (0.0)	2.166 78
8.0	0.460 75 (78.3)	2.123 16 (0.1)	2.125 00 (0.0)	2.125 04
10.0	0.371 28 (82.3)	2.098 81 (0.1)	2.100 00 (0.0)	2.100 02
15.0	0.249 22 (87.9)	2.066 13 (0.0)	2.066 67 (0.0)	2.066 67
20.0	0.187 28 (90.9)	2.049 70 (0.0)	2.050 00 (0.0)	2.050 00

[a] References 13 and 14.

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.

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APPENDIX

The following position-space interpretation is possible for the functions $S^{nlm}_{n'l'm'}(\mathbf{R})$ and $W^{nlm}_{n'l'm'}(\mathbf{R})$ introduced in Sec. II.

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

$$u_{nlm}(\mathbf{r}-\mathbf{R}) \overset{\text{FT}}{\leftrightarrow} \exp(-i\mathbf{p}\cdot\mathbf{R})\Phi_{nlm}(\mathbf{p}), \tag{A1}$$

$$|\mathbf{r}|^{-1}u_{nlm}(\mathbf{r}) \overset{\text{FT}}{\leftrightarrow} (2\pi^2)^{-1}\int |\mathbf{p}-\mathbf{p}'|^{-2}\Phi_{nlm}(\mathbf{p}')d\mathbf{p}'$$
$$= [2p_0^{3/2}/(p^2+p_0^2)]\,Y_{nlm}(\Omega). \tag{A2}$$

Therefore we obtain

$$\int u^*_{n'l'm'}(\mathbf{r}-\mathbf{R})|\mathbf{r}|^{-1}u_{nlm}(\mathbf{r})d\mathbf{r}$$
$$= \int [\exp(-i\mathbf{p}\cdot\mathbf{R})\Phi_{n'l'm'}(\mathbf{p})]^*$$
$$\times [2p_0^{3/2}/(p^2+p_0^2)]\,Y_{nlm}(\Omega)d\mathbf{p}$$

$$= p_0 \int \exp(i\mathbf{p}\cdot\mathbf{R}) Y^*_{n'l'm'}(\Omega) Y_{nlm}(\Omega) d\Omega$$

$$= p_0 S^{nlm}_{n'l'm'}(\mathbf{R}), \tag{A3}$$

which implies that the function $S^{nlm}_{n'l'm'}(\mathbf{R})$ is proportional to the nuclear attraction integral in position space over the hydrogenic functions. As a result,

$$S^{nlm}_{n'l'm'}(\mathbf{R}) \to 0 \text{ as } |\mathbf{R}| \to \infty. \tag{A4}$$

Alternative correspondence was given by Shibuya and Wulfman[4] (see also Refs. 5 and 9). The result is

$$S^{nlm}_{n'l'm'}(\mathbf{R}) = (1/2) \sum_{\nu\lambda\mu} (2\pi/p_0)^{3/2} V^{nlm}_{n'l'm',\nu\lambda\mu} u_{\nu\lambda\mu}(\mathbf{R}), \tag{A5}$$

$$V^{nlm}_{n'l'm',\nu\lambda\mu} = (2\pi^2)^{1/2} \int [2Y_{100}(\Omega) + Y_{200}(\Omega)] Y_{nlm}(\Omega) \times Y^*_{n'l'm'}(\Omega) Y^*_{\nu\lambda\mu}(\Omega) d\Omega, \tag{A6}$$

and $S^{nlm}_{n'l'm'}(\mathbf{R})$ is expressible by a linear combination of a finite number of position-space hydrogenic functions.

Similarly, considering another correspondence

$$|\mathbf{r}-\mathbf{R}|^{-1} u_{nlm}(r) \overset{\text{FT}}{\leftrightarrow} (2\pi^2)^{-1} \int |\mathbf{p}-\mathbf{p}'|^{-2} \exp[-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}] \Phi_{nlm}(\mathbf{p}') d\mathbf{p}' = [2p_0^{3/2}/(p^2+p_0^2)] \exp(-i\mathbf{p}\cdot\mathbf{R}) \times \sum_{\nu\lambda\mu} \nu^{-1} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) Y_{\nu\lambda\mu}(\Omega), \tag{A7}$$

we have

$$\int u^*_{n'l'm'}(\mathbf{r}) |\mathbf{r}-\mathbf{R}|^{-1} u_{nlm}(\mathbf{r}) d\mathbf{r}$$

$$= p_0 \int \left[\sum_{\nu\lambda\mu} \nu^{-1} S^{nlm}_{\nu\lambda\mu}(\mathbf{R}) Y_{\nu\lambda\mu}(\Omega) \right] \times [\exp(i\mathbf{p}\cdot\mathbf{R}) Y_{n'l'm'}(\Omega)]^* d\Omega$$

$$= p_0 W^{nlm}_{n'l'm'}(\mathbf{R}). \tag{A8}$$

Thus the function $W^{nlm}_{n'l'm'}(\mathbf{R})$ is proportional to another kind of nuclear attraction integral in position space, and

$$W^{nlm}_{n'l'm'}(\mathbf{R}) \to 0 \text{ as } |\mathbf{R}| \to \infty. \tag{A9}$$

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

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