General procedure for determination of shielded diatomic orbitals

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The determination procedure for shielded diatomic orbitals which are eigenfunctions of the two-center problem is generalized for any polynomial form of the separated parametric shielding potentials. The matrix technique using a Newton-Raphson scheme for simultaneous resolution of the separated equations, and the matrix elements of the general shielding potential are presented.

In previous papers[1,2] the basic procedure for the determination of shielded diatomic orbitals (SDO), as exact solutions of the one-electron two-center Schrödinger equation with a parametric shielding potential with cylinder symmetry, has been investigated. This comment presents an extension of the previously described procedure so that the empirical shielding potential can be given a more flexible form.

I. GENERALIZED PROCEDURE

Hereafter the notations of Refs. 1 and 2 will be used. Shielded diatomic orbitals ψ_i are eigenfunctions in prolate spheroidal coordinates (λ, μ, φ) of the following effective Hamiltonian, corresponding to orbital energies ϵ_i,[3]

$$[\Delta_i + 2(Z_A/r_{iA} + Z_B/r_{iB}) - V(i) + 2\epsilon_i]\Psi_i = 0 . \quad (1)$$

$V(i)$ is a one-electron shielding potential representing the average interelectronic repulsion due to the other electrons:

$$V(\lambda_i, \mu_i) = \frac{4[F(\lambda_i) + G(\mu_i)]}{R^2(\lambda_i^2 - \mu_i^2)} , \quad (2a)$$

where

$$F(\lambda_i) = R \sum_{j=0}^{J} A_j(i)\lambda_i^j , \quad G(\mu_i) = R \sum_{j=0}^{J} B_j(i)\mu_i^j . \quad (2b)$$

The $A_j(i)$ and $B_j(i)$ are parameters that could be determined either by electrostatic considerations[2] or by a variational procedure. Up to now[1,2,4] truncated expansions ($J = 0, 3$) have been assumed for the arbitrary functions $F(\lambda)$ and $G(\mu)$. In the present paper, the resolution procedure for Eq. (1) is described in the general case where $F(\lambda)$ and $G(\mu)$ are polynomials of any degree J in λ and μ, respectively ($J = 0, \infty$).

Assuming for $V(i)$ the general form defined by (2), Eq. (1) remains separable in prolate spheroidal coordinates, and we can write (the index i being omitted)

$$\Psi(\lambda, \mu, \varphi) = \Lambda(\lambda)M(\mu, \varphi) = \Lambda(\lambda)S(\mu)e^{\pm im\varphi} .$$

The functions $M(\mu, \varphi)$ and $\Lambda(\lambda)$ are, respectively, solutions of the following pair of differential equations:

$$\left\{\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right] - \frac{m^2}{1-\mu^2} - \sum_{j=0}^{J} B'_j \mu^j - \mathfrak{A}\right\} M(\mu, \varphi) = 0 , \quad (3)$$

$$\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right] - \frac{m^2}{\lambda^2-1} - \sum_{j=0}^{J} A'_j \lambda^j + \mathfrak{A}\right\} \Lambda(\lambda) = 0 , \quad (4)$$

where

$$B'_1 = R(Z_A - Z_B + B_1), \quad B'_2 = RB_2 - p^2$$

$$A'_1 = -R(Z_A + Z_B - A_1), \quad A'_2 = RA_2 + p^2 .$$

$B'_j = B_j$; $A'_j = A_j$ for $j = 0$ and $j = 3, J$ (Ref. 5), p^2 is the energy parameter: $\epsilon = -2p^2/R^2$, and the separation constant $\mathfrak{A}$ is the eigenvalue of an invariant operator.[6,7]

A. Matrix equations

(i) The function $M(\mu, \varphi)$ is expanded as a linear combination of spherical harmonics:

$$M(\mu, \varphi) = \sum_{k=m}^{\infty} f_k^m Y_k^m(\mu, \varphi) . \quad (5)$$

The general expansion for $\mu^j Y_k^m(\mu, \varphi)$ in terms of spherical harmonics[8] and the linear independence property of the spherical harmonics lead, in a straightforward manner, to the following difference equation defining the f_k^m coefficients

$$f_k^m[-k(k+1)-\mathfrak{A}]+(-)^{m+1}\left[\sum_{j=0}^{J} B'_j \sum_{t=0,2}^{j} f_{k\pm t}^m[(2k+1)(2k\pm 2t+1)]^{1/2} \sum_{n=(t-v)/2}^{(j-v)/2} D(n,(j-v)/2) \times \begin{pmatrix} 2n+v & k & k\pm t \\ 0 & m & -m \end{pmatrix}\begin{pmatrix} 2n+v & k & k\pm t \\ 0 & 0 & 0 \end{pmatrix}\right]=0, \quad (6)$$

for all $k \geq m$, where

$$v \equiv j \bmod 2,$$

$$D(n,(j-v)/2)=\frac{2^{2n+v}(4n+1+2v)\,j![(j+v)/2+n]!}{(j+v+2n+1)![(j-v)/2-n]!}. \quad (7)$$

If (3) is even in the variable μ (homonuclear case with $B_{2j+1}=0$), the values of k jump by steps of two units. When truncating the expansion (5) ($k=m,K$) the set of difference Eqs. (6) is concisely expressed by the following matrix equation:

$$[\mathfrak{F}(p,\mathfrak{A})]\,|f|=0. \quad (8)$$

The expressions for the nonvanishing elements of the symmetric $(K-m+1)$-dimensional, $(2J+1)$-diagonal $[\mathfrak{F}(p,\mathfrak{A})]$ matrix are directly derived from (6).

(ii) Alternatively, an Hylleraas-like expansion has been chosen for the $\Lambda(\lambda)$ function:

$$\Lambda(\lambda)=e^{-p(\lambda-1)}[2p(\lambda-1)]^{m/2}\sum_{s=m/2}^{\infty} C_n \mathfrak{L}_n^m[2p(\lambda-1)], \quad (9)$$

where $n=s-m/2$ is an integer and $\mathfrak{L}_n^m(x)$ is the normalized Laguerre polynomial.

Expanding the product $x^j\mathfrak{L}_n^m(x)$ in terms of normalized Laguerre polynomials, and using the linear-independence property of the $\mathfrak{L}_n^m(x)$ functions, one obtains the following difference equation defining the expansion coefficients C_n:

$$\sum_{j=0}^{J} C_{n\pm j}\mathcal{G}_{\pm j}+pm^2 d_n=0, \quad \text{for all } n\geq 0, \quad (10)$$

where

$$\begin{aligned}
\mathcal{G}_0 &= \tfrac{1}{2}m(\tfrac{1}{2}m+1)+n-2p(2n+m+1) \\
&\quad -(n+\tfrac{1}{2}m+1-p)\mathfrak{C}_n^1+\tfrac{1}{4}\mathfrak{C}_n^2+W(0,0), \\
\mathcal{G}_{-1} &= -(n+\tfrac{1}{2}m-p)\mathfrak{C}_{n-1}^1+\tfrac{1}{4}\mathfrak{C}_{n-1}^2+W(1,-1), \\
\mathcal{G}_1 &= -(n+\tfrac{1}{2}m+1-p)\mathfrak{C}_{n+1}^1+\tfrac{1}{4}\mathfrak{C}_{n+1}^2+W(1,1), \\
\mathcal{G}_{\pm 2} &= \tfrac{1}{4}\mathfrak{C}_{n\pm 2}^2+W(2,\pm 2), \\
\mathcal{G}_{\pm l} &= W(l,\pm l) \quad \text{for } l=3,J, \\
W(l,k) &= \sum_{j=l}^{J} A'_j \sum_{i=l}^{j} \frac{1}{(2p)^i}\binom{j}{i}\mathfrak{C}_{n+k}^i.
\end{aligned} \quad (11)$$

The $\mathfrak{C}_{n\pm k}^i$ expansion coefficients are defined by the following recursion formula[9]:

$$\begin{aligned}
\mathfrak{C}_{n\pm k}^i &= (2n\pm 2k+m+1)\mathfrak{C}_{n\pm k}^{i-1}-[(n\pm k)(n\pm k+m)]^{1/2}\mathfrak{C}_{n\pm k-1}^{i-1} \\
&\quad -[(n\pm k+1)(n\pm k+m+1)]^{1/2}\mathfrak{C}_{n\pm k+1}^{i-1} \\
&\qquad \text{for all } k=0,1,\cdots i, \quad (12a)
\end{aligned}$$

with the initial condition

$$\mathfrak{C}_n^0=1 \quad (12b)$$

and they satisfy the following condition:

$$\mathfrak{C}_{n\pm k}^i=0 \quad \text{for } k>i. \quad (12c)$$

When truncating the expression (9) ($n=0,N$) the set of difference equations (10) can be expressed by the following matrix equation:

$$[\mathcal{Y}(p,\mathfrak{A})]\,|c|=0, \quad (13a)$$

where

$$\begin{aligned}
&[\mathcal{Y}(p,\mathfrak{A})]=[\mathcal{R}(p,\mathfrak{A})]+pm^2[\mathfrak{B}(p)]^{-1}, \\
&|c|=[\mathfrak{B}(p)]\,|d|.
\end{aligned} \quad (13b)$$

The expressions of the nonvanishing elements of the symmetric, $(N+1)$-dimensional, $(2J+1)$-diagonal $[\mathcal{R}(p,\mathfrak{A})]$ matrix are directly derived from (10) and (11).

For the particular cases $J=2$ and 3, the expressions obtained for the nonvanishing elements of both $[\mathfrak{F}(p,\mathfrak{A})]$ and $[\mathcal{R}(p,\mathfrak{A})]$ matrices are available from Refs. 1 and 2.

B. Simultaneous resolution of the separated two-center equations

The characteristic values $(\mathfrak{A},p)$ of a shielded diatomic orbital, common to both matrix equations (8) and (13a) are determined by the iterative Newton-Raphson process.[2] Then, the expansion coefficients vector $|f|$ and $|c|$ are obtained by diagonalizing the $[\mathfrak{F}(p,\mathfrak{A})]$ and $[\mathcal{Y}(p,\mathfrak{A})]$ matrices, respectively.

II. MATRIX ELEMENTS $\mathcal{V}_{ab}$ OF THE SHIELDING POTENTIAL $V(\lambda,\mu)$

$$\mathcal{V}_{ab}=\frac{R^3}{8}\int_0^{2\pi}d\varphi\int_{-1}^{+1}d\mu\int_1^{\infty}d\lambda(\lambda^2-\mu^2)\,\Psi_a^*(\lambda,\mu,\varphi) \times V(\lambda,\mu)\Psi_b(\lambda,\mu,\varphi), \quad (14)$$

where $V(\lambda, \mu)$ is defined by (2). Thus (14) can be written

$$v_{ab} = \frac{R^2}{2}\left(T^{(0)}_{a,b}\sum_{j=0}^{J} B_j U^{(j)}_{a,b} + U^{(0)}_{a,b}\sum_{j=0}^{J} A_j T^{(j)}_{a,b}\right), \quad (15)$$

where

$$T^{(j)}_{a,b} = \int_1^\infty d\lambda\, \Lambda_a(\lambda)\lambda^j \Lambda_b(\lambda)\,, \quad (16)$$

$$U^{(j)}_{a,b} = \int_0^{2\pi} d\varphi \int_{-1}^{+1} d\mu\, M^*_a(\mu, \varphi)\mu^j M_b(\mu, \varphi)\,. \quad (17)$$

Since the $M(\mu, \varphi)$ functions are expanded in terms of spherical harmonics, the basic integrals $U^{(j)}_{a,b}$ can be expressed in terms of $3j$ Wigner coefficients:

$$U^{(j)}_{a,b} = \sum_{i=0}^{(j-v)/2} D(i, (j-v)/2) X_{a,b}(2i+v, 0)\,, \quad (18)$$

where $v \equiv j \bmod 2$

$$X_{a,b}(l, m) = (-)^{m_a} \sum_{k_a=m_a}^{K_a} \sum_{k_b=m_b}^{K_b} f^{m_a}_{k_a} f^{m_b}_{k_b} [(2k_a+1)(2k_b+1)]^{1/2} \times \begin{pmatrix} k_a & l & k_b \\ -m_a & m & m_b \end{pmatrix} \begin{pmatrix} k_a & l & k_b \\ 0 & 0 & 0 \end{pmatrix}, \quad (19)$$

and D is defined by (7).

The off-diagonal matrix elements $T^{(j)}_{a,b}$ can be evaluated by means of a Gaussian quadrature, while the diagonal matrix elements $T^{(j)}_{a,a}$ are analytically determined:

$$T^{(j)}_{a,a} = \frac{1}{2p}\sum_{i=0}^{j}\binom{j}{i}\frac{1}{(2p)^i} I_i\,, \quad (20)$$

where

$$I_i = \sum_{n=0}^{N}\sum_{u=0}^{N} c_n c_u \int_0^\infty e^{-x} x^i x^m \mathfrak{L}^m_n(x)\mathfrak{L}^m_u(x)\, dx\,,$$

with $x = 2p(\lambda - 1)$, $m = m_a$.

Using the functional relation

$$x^i \mathfrak{L}^m_n(x) = \sum_{k=0}^{i} \mathfrak{C}^i_{n\pm k}\mathfrak{L}^m_{n\pm k}(x)\,,$$

one obtains

$$I_i = \sum_{n=0}^{N}\left(c_n^2 \mathfrak{C}^i_n + 2\sum_{k=1}^{i} c_n c_{n+k}\mathfrak{C}^i_{n+k}\right), \quad (21)$$

where the coefficients $\mathfrak{C}^i_{n+k}$ for $k=0$, i are defined by the expressions (12). The expressions obtained for $T^{(j)}_{a,a}$ are available for $j=0, 4$ in Refs. 1 and 2.

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