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Two Electron Diatomic Molecules. II. Extension and Refinement of the James-Coolidge Method and the Computer Program "MADAM"

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The systematic formulation to calculate adiabatically the energies and wave functions of two electron two nucleus systems with any nuclear charge by the James-Coolidge method is given. This formulation can be applied, in principle, to any state of the hydrogen-like molecule at any internuclear distance. The computer program to perform the numerical work based on this formulation is constructed and named "MADAM".

§ 1. Introduction

In the previous report[1], the computer program to obtain the energies and wave functions in the singlet or the triplet Σ^+ states of the two electron diatomic molecules with any nuclear charge by the James-Coolidge method[2] was elaborated. This article pursues the extension of the previous work to any state of the hydrogen-like molecule. The reasons to undertake this research in spite of a series of excellent works by Kołos, Wolniewicz, and their collaborators[3] are i) to make the James-Coolidge type wave functions available at our disposal, ii) to confirm the accuracy of the results obtained by the above mentioned authors, and iii) to investigate the applicability of the method for a wide range of the value of the internuclear distance in various states.

§ 2. Formulation

Using the atomic units, the adiabatic Hamiltonian is given by

$$
\begin{aligned}
&H=T+U,\\
&T=-(\Delta_1+\Delta_2)/2,\\
&U=-Z_a/r_{a1}-Z_b/r_{b1}-Z_a/r_{a2}-Z_b/r_{b2}+1/r_{12}+Z_aZ_b/R,
\end{aligned}
\tag{1}
$$

where the notations are self-explanatory[1].

Using the elliptical coordinates λ, μ, φ, and $\rho=2r_{12}/R$, the Hamiltonian (1) is expressed as

$$H=T+(Z_a+Z_b)U^{(1)}/2+(Z_a-Z_b)U^{(2)}/2+U^{(3)}+Z_aZ_b/R.$$

where

$$T=T'/R^2,\quad U^{(1)}=U'^{(1)}/R,\quad U^{(2)}=U'^{(2)}/R,\quad U^{(3)}=U'^{(3)}/R,$$

and

$$
\begin{aligned}
&T'=-R^2(\Delta_1+\Delta_2)/2,\\
&U'^{(1)}=-4\lambda_1/(\lambda_1^2-\mu_1^2)-4\lambda_2/(\lambda_2^2-\mu_2^2),\\
&U'^{(2)}=4\mu_1/(\lambda_1^2-\mu_1^2)+4\mu_2/(\lambda_2^2-\mu_2^2),\\
&U'^{(3)}=2/\rho.
\end{aligned}
\tag{2}
$$

In order to be applicable to any state and any R, the basis functions of the James-Coolidge type wave function should be generalized to have sufficient flexibility and proper symmetry. In the first place, we introduce the functions

$$
\begin{aligned}
&\phi(m,n,j,k,p,l_1,l_2\ ;\ \alpha_1,\alpha_2,\beta_1,\beta_2)\equiv\phi\equiv(m,n,j,k,p,l_1,l_2\ ;\ \alpha_1,\alpha_2,\beta_1,\beta_2)\\
&\quad=(1/2\pi)(2/R)^3\exp[-\alpha_1\lambda_1-\alpha_2\lambda_2-\beta_1\mu_1-\beta_2\mu_2]\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^p\\
&\quad\times M_1^{|l_1|}M_2^{|l_2|}\exp[il_1\varphi_1+il_2\varphi_2],
\end{aligned}
\tag{3}
$$

where

$$M_i=[(\lambda_i^2-1)(1-\mu_i^2)]^{1/2},\qquad (i=1,2).$$

Next, we define the functions $\psi(m,n,j,k,p,l_1,l_2\ ;\ \alpha_1,\alpha_2,\beta_1,\beta_2)\equiv\psi$ as follows:

$$
\begin{aligned}
&\psi=(\phi+\bar{\phi})/2, && \text{for } \Sigma^+ \text{ state},\\
&\psi=(\phi-\bar{\phi})/(2i), && \text{for } \Sigma^- \text{ state},\\
&\psi=\phi, && \text{otherwise},
\end{aligned}
\tag{4}
$$

where $\bar{\phi}$ is the complex conjugate of ϕ.

In the homopolar case, the symmetry adapted basis functions $\Phi(m,n,j,k,p,l_1,l_2\ ;\ \alpha_1,\alpha_2,\beta_1,\beta_2)$ are constructed by using

$$\begin{aligned}
\psi_A &= \psi(m, n, j, k, p, l_1, l_2 \ ; \ \alpha_1, \alpha_2, \beta_1, \beta_2), \\
\psi_B &= \psi(m, n, j, k, p, l_1, l_2 \ ; \ \alpha_1, \alpha_2, -\beta_1, -\beta_2), \\
\psi_C &= \psi(n, m, k, j, p, l_2, l_1 \ ; \ \alpha_2, \alpha_1, \beta_2, \beta_1), \\
\psi_D &= \psi(n, m, k, j, p, l_2, l_1 \ ; \ \alpha_2, \alpha_1, -\beta_2, -\beta_1),
\end{aligned} \tag{5}$$

as follows

$$\begin{aligned}
\Phi &= [(\psi_A + \psi_C) + (-1)^{j+k+l_1+l_2}(\psi_B + \psi_D)], && \text{for singlet } g \text{ state}, \\
\Phi &= [(\psi_A + \psi_C) - (-1)^{j+k+l_1+l_2}(\psi_B + \psi_D)], && \text{for singlet } u \text{ state}, \\
\Phi &= [(\psi_A - \psi_C) + (-1)^{j+k+l_1+l_2}(\psi_B - \psi_D)], && \text{for triplet } g \text{ state}, \\
\Phi &= [(\psi_A - \psi_C) - (-1)^{j+k+l_1+l_2}(\psi_B - \psi_D)], && \text{for triplet } u \text{ state},
\end{aligned} \tag{6}$$

where normalization factors are omitted for simplicity.

In the heteropolar case, since g, u symmetry is missing, merely the combinations $\psi_A \pm \psi_C$ or $\psi_B \pm \psi_D$ is sufficient. It is to be noted that four parameters α_1, α_2, β_1, and β_2 are introduced in the exponent of Φ. Moreover, not only ρ but also φ_1 and φ_2 can be involved even in the Σ states and so the basis functions are more flexible than the original ones adopted by James and Coolidge.

The matrix elements of the Hamiltonian H and the unity S with respect to the basis function Φ's can be obtained easily by those with respect to the function ϕ's. The latter matrix elements can be expressed by the auxiliary function X's as shown in Appendix A. The derivation of the auxiliary function X's by using Kotani, Amemiya, and Simose's auxiliary functions[4] is shown in Appendix B.

§ 3. Computer program "MADAM"

A package of computer programs named MADAM (the **M**ost **A**ccurate **Di**A**tomic** **M**olecular calculation) is constructed by employing the method explained in § 2 and Appendices A and B. MADAM consists of several job steps; calculation of the values of auxiliary functions, construction of the matrix elements, and calculation of the energy and wave function. A lot of machine time is required to optimize the non-linear parameters α_1, α_2, β_1 and β_2 and to find the best set of the basis functions. As a test run, MADAM has been applied for a number of problems and good agreement with the previous results[3] has been found. Besides the full application of MADAM, we also undertake as a natural extension the calculation of the polarizability of the H_2 like molecules in any state. The details of the application will be published elsewhere.

References

[1] N. Ueda, H. Sato, E. Ishiguro and T. Takezawa: Nat. Sci. Rep. Ochanomizu Univ. **27** (1976) 33, referred to as I.
[2] H.M. James and A.S. Coolidge: J. chem. Phys. **1** (1933) 825.
[3] for example, W. Kołos and J. Rychlewski: Acta Physica Polonica **A53** (1978) 281.
[4] M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura: *Tables of Molecular Integrals* (Maruzen, Tokyo, 1963).

Appendix A. The matrix elements of T', $U'^{(1)}$, $U'^{(2)}$, $U'^{(3)}$, and S with respect to the function ϕ.

The matrices of T, U, and S with respect to $\phi_f=\phi(m, n, j, k, p, l_1, l_2\,;\ \alpha_1, \alpha_2, \beta_1, \beta_2)$ and $\phi_g=\phi(m', n', j', k', p', l_1', l_2'\,;\ \alpha_1', \alpha_2', \beta_1', \beta_2')$ have nonzero elements only when

$$l_1+l_2=l_1'+l_2', \tag{A1}$$

and these nonzero matrix elements can be expressed in terms of the auxiliary functions of the following form

$$\begin{aligned} &X(M, M, N, J, K, P, L_1, L_2, \gamma\ ;\ A_1, A_2, B_1, B_2)\\ &\quad=(1/2\pi)^2\int\exp[-A_1\lambda_1-A_2\lambda_2-B_1\mu_1-B_2\mu_2]\lambda_1^M\lambda_2^N\mu_1^J\mu_2^K\rho^P\\ &\qquad\times M_1^{L_1}M_2^{L_2}\exp[i\gamma(\varphi_1-\varphi_2)]\mathrm{d}\lambda_1\mathrm{d}\lambda_2\mathrm{d}\mu_1\mathrm{d}\mu_2\mathrm{d}\varphi_1\mathrm{d}\varphi_2. \end{aligned} \tag{A2}$$

The method of calculation of these auxiliary functions is given in Appendix B. In what follows, we shall adopt the usual abbreviation for the arguments of the auxiliary functions[1-2]. For example,

$$\begin{aligned} S_{fg}=&X(m+m'+2, n+n'+2, j+j', k+k', p+p', |l_1|+|l_1'|, |l_2|+|l_2'|,\\ &-l_1+l_1'\ ;\ \alpha_1+\alpha_1', \alpha_2+\alpha_2', \beta_1+\beta_1', \beta_2+\beta_2')\\ &-X(m+m'+2, n+n', j+j', k+k'+2, p+p', |l_1|+|l_1'|, |l_2|+|l_2'|,\\ &-l_1+l_1'\ ;\ \alpha_1+\alpha_1', \alpha_2+\alpha_2', \beta_1+\beta_1', \beta_2+\beta_2')\\ &-X(m+m', n+n'+2, j+j'+2, k+k', p+p', |l_1|+|l_1'|, |l_2|+|l_2'|,\\ &-l_1+l_1'\ ;\ \alpha_1+\alpha_1', \alpha_2+\alpha_2', \beta_1+\beta_1', \beta_2+\beta_2')\\ &+X(m+m', n+n', j+j'+2, k+k'+2, p+p', |l_1|+|l_1'|, |l_2|+|l_2'|,\\ &-l_1+l_1'\ ;\ \alpha_1+\alpha_1', \alpha_2+\alpha_2', \beta_1+\beta_1', \beta_2+\beta_2')\\ =&X(22000,000)-X(20020,000)-X(02200,000)+X(00220,000). \end{aligned} \tag{A3}$$

Further, when the last three arguments of X in Eq. (A3) are equal to zero, these arguments are omitted, e. g., $X(22000,000)=X(22000)$. Then,

$$U'^{(1)}_{fg}=-4\{X(12000)-X(10020)+X(21000)-X(01200)\}, \tag{A4}$$

$$U'^{(2)}_{fg}=4\{X(02100)-X(00120)+X(20010)-X(00210)\}, \tag{A5}$$

$$U'^{(3)}_{fg}=2\{X(2200-1)-X(2002-1)-X(0220-1)+X(0022-1)\}. \tag{A6}$$

For the kinetic energy operator, we have

$$T'=T'_1+T'_2,$$

$$T'_i=-R^2\Delta_i/2, \qquad (i=1,2). \tag{A7}$$

The matrix elements of T'_1 consists of four parts,

$$T'_{1fg}=\sum_{s=1}^{4} T'^{(s)}_{1fg}, \qquad (s=1,2,3,4). \tag{A8}$$

After a somewhat lengthy calculation, we have

$$\begin{aligned}
T'^{(1)}_{1fg}=&-[(\alpha_1-\alpha'_1)^2\{X(22000)-X(20020)\}\\
&-(\beta_1-\beta'_1)^2\{X(02200)-X(00220)\}\\
&-\{2(\alpha_1+\alpha'_1)+(\alpha_1-\alpha'_1)(2(m-m')+(p-p')+2(|l_1|-|l'_1|))\}\\
&\times\{X(12000)-X(10020)\}\\
&+\{2(\beta_1+\beta'_1)+(\beta_1-\beta'_1)(2(j-j')+(p-p')+2(|l_1|-|l'_1|))\}\\
&\times\{X(02100)-X(00120)\}\\
&+2(\alpha_1-\alpha'_1)(m-m')\{X(-12000)-X(-10020)\}\\
&-2(\beta_1-\beta'_1)(j-j')\{X(02-100)-X(00-120)\}\\
&-\{(m-m')^2-(m+m')\}\{X(-22000)-X(-20020)\}\\
&+\{(j-j')^2-(j+j')\}\{X(02-200)-X(00-220)\}\\
&+\{-(\alpha_1-\alpha'_1)^2+(\beta_1-\beta'_1)^2+(m-m')^2-(j-j')^2+(m+m')-(j+j')\\
&+(m-m'-j+j')(p-p'+2(|l_1|-|l'_1|))\}\{X(02000)\\
&-X(00020)\}]/2,
\end{aligned} \tag{A9}$$

$$\begin{aligned}
T'^{(2)}_{1fg}=&(p-p')[(\alpha_1-\alpha'_1)\{X(3200-2)-X(3002-2)-X(1400-2)\\
&-X(1220-2)+X(1022-2)+X(1004-2)+2X(0311-2)\\
&-2X(0113-2)\}+(\beta_1-\beta'_1)\{X(2210-2)-X(2012-2)\\
&+X(0410-2)-X(0230-2)+X(0032-2)-X(0014-2)\\
&-2X(1301-2)+2X(1103-2)\}\\
&+(m-m'-j+j')\{X(0400-2)-X(0004-2)\}
\end{aligned}$$

$$
\begin{aligned}
&-2(m-m')\{X(-1311-2)-X(-1113-2)\}\\
&+2(j-j')\{X(13-11-2)-X(11-13-2)\}]/2\\
&-[\{(p-p')(m-m'+j-j')+(p-p')^2+(p+p')\\
&+2(p-p')(|l_1|-|l_1'|)\}\{X(2200-2)-X(2002-2)\\
&-X(0220-2)+X(0022-2)\}]/2\,, \qquad \text{(A10)}
\end{aligned}
$$

$$
\begin{aligned}
T_{1fg}'^{(3)}=&(p-p')[(|l_1|-|l_1'|+l_1+l_1')\{X(2200-2,\,-111)\\
&-X(2002-2,\,-111)-X(0220-2,\,-111)+X(0022-2,\,-111)\}\\
&+(|l_1|-|l_1'|-l_1-l_1')\{X(2200-2,\,-11-1)-X(2002-2,\,-11-1)\\
&-X(0220-2,\,-11-1)+X(0022-2,\,-11-1)\}]/2\,, \qquad \text{(A11)}
\end{aligned}
$$

$$
\begin{aligned}
T_{1fg}'^{(4)}=&\{(l_1+l_1')^2-(|l_1|-|l_1'|)^2\}\{X(22000,\,-200)-X(20020,\,-200)\\
&-X(02200,\,-200)+X(00220,\,-200)\}/2\,. \qquad \text{(A12)}
\end{aligned}
$$

The matrix elements of T_2' can be obtained from the above equations, *mutatis mutandis.*

Appendix B. Auxiliary function $X(M, N, J, K, P, L_1, L_2, \gamma\,;\, A_1, A_2, B_1, B_2)$.

The auxiliary function $X(M, N, J, K, P, L_1, L_2, \gamma\,;\, A_1, A_2, B_1, B_2)$ is defined by Eq. (A2). The four parameters A_1, A_2, B_1, and B_2 are not shown explicitly in this appendix. Here, the arguments M, N, J, K, P, L_1, L_2, and γ are integers and

$$M, N, J, K, L_1, L_2 \geqq 0, \qquad P \geqq -1, \qquad L_1, L_2 \geqq |\gamma|\,.$$

Using the relation

$$
\begin{aligned}
\rho^2=&\lambda_1^2+\lambda_2^2+\mu_1^2+\mu_2^2-2-2\lambda_1\lambda_2\mu_1\mu_2\\
&-M_1M_2\exp[i(\varphi_1-\varphi_2)]-M_1M_2\exp[-i(\varphi_1-\varphi_2)], \qquad \text{(B1)}
\end{aligned}
$$

the following recurrence formula

$$
\begin{aligned}
&X(M, N, J, K, P+2, L_1, L_2, \gamma)\\
&=X(M+2, N, J, K, P, L_1, L_2, \gamma)+X(M, N+2, J, K, P, L_1, L_2, \gamma)\\
&+X(M, N, J+2, K, P, L_1, L_2, \gamma)+X(M, N, J, K+2, P, L_1, L_2, \gamma)\\
&-2X(M, N, J, K, P, L_1, L_2, \gamma)-2X(M+1, N+1, J+1, K+1, P, L_1, L_2, \gamma)\\
&-X(M, N, J, K, P, L_1+1, L_2+1, \gamma+1)\\
&-X(M, N, J, K, P, L_1+1, L_2+1, \gamma-1) \qquad \text{(B2)}
\end{aligned}
$$

is derived immediately. Therefore, the function X with $P \geqq 1$ can be obtained from X's with $P=-1$ and 0.

For $P=-1$, the Neumann expansion of $1/\rho$[4] is substituted into Eq. (A2), and the expression

$$\begin{aligned} &X(M, N, J, K, -1, L_1, L_2, \gamma) \\ &\quad = (-1)^{|\gamma|} \sum_{\tau=|\gamma|}^{\infty} (2\tau+1)\{(\tau-|\gamma|)!/(\tau+|\gamma|)!\}^2 \\ &\qquad \times w(\tau, |\gamma|, M, N, (L_1-|\gamma|)/2, (L_2-|\gamma|)/2 \ ; \ A_1, A_2) \\ &\qquad \times g(\tau, |\gamma|, J, (L_1-|\gamma|)/2 \ ; \ B_1) g(\tau, |\gamma|, K, (L_2-|\gamma|)/2 \ ; \ B_2) \end{aligned} \tag{B3}$$

is obtained, where

$$\begin{aligned} &w(\tau, \nu, m, n, s, t \ ; \ \alpha_1, \alpha_2) \\ &\quad = \int_1^{\infty}\int_1^{\infty} \exp[-\alpha_1\lambda_1 - \alpha_2\lambda_2] \lambda_1^m \lambda_2^n Q_\tau^\nu(\lambda_>) P_\tau^\nu(\lambda_<) \\ &\qquad \times (\lambda_1^2-1)^{\nu/2+s} (\lambda_2^2-1)^{\nu/2+t} \mathrm{d}\lambda_1 \mathrm{d}\lambda_2, \end{aligned} \tag{B4}$$

$$g(\tau, \nu, j, s \ ; \ \beta) = \int_{-1}^{1} \exp[-\beta\mu] \mu^j P_\tau^\nu(\mu) (1-\mu^2)^{\nu/2+s} \mathrm{d}\mu, \tag{B5}$$

and $\lambda_>$ denotes the larger one of λ_1 and λ_2, $\lambda_<$ the smaller one. In Eqs. (B4) and (B5), s and t are nonnegative integers, and, therefore, the functions w and g can be easily expressed by the functions

$$\begin{aligned} &W_\tau^\nu(m, n \ ; \ \alpha_1, \alpha_2) \\ &\quad = \int_1^{\infty}\int_1^{\infty} \exp[-\alpha_1\lambda_1 - \alpha_2\lambda_2] \lambda_1^m \lambda_2^n Q_\tau^\nu(\lambda_>) P_\tau^\nu(\lambda_<) \\ &\qquad \times [(\lambda_1^2-1)(\lambda_2^2-1)]^{\nu/2} \mathrm{d}\lambda_1 \mathrm{d}\lambda_2, \end{aligned} \tag{B6}$$

and

$$G_\tau^\nu(j \ ; \ \beta) = \int_{-1}^{1} \exp[-\beta\mu] \mu^j P_\tau^\nu(\mu) (1-\mu^2)^{\nu/2} \mathrm{d}\mu. \tag{B7}$$

These functions are familiar in the literatures of molecular integrals and the method of their calculation is given by Kotani *et. al.*[4]

For $P=0$, the function X has nonzero value only when $\gamma=0$, and hence only the X's with even L_1 and L_2 are required,

$$\begin{aligned} &X(M, N, J, K, 0, L_1, L_2, 0) \\ &\quad = a(M, L_1/2 \ ; \ A_1) a(N, L_2/2 \ ; \ A_2) b(J, L_1/2 \ ; \ B_1) b(K, L_2/2 \ ; \ B_2), \end{aligned} \tag{B8}$$

where

$$a(m, l \ ; \ \alpha) = \int_1^{\infty} \exp[-\alpha\lambda] \lambda^m (\lambda^2-1)^l \mathrm{d}\lambda, \tag{B9}$$

and

$$b(j, l\ ;\ \beta)=\int_{-1}^{1}\exp[-\beta\mu]\mu^{j}(1-\mu^{2})^{l}\mathrm{d}\mu. \tag{B10}$$

Again, the functions a and b can be expressed easily by the familiar functions[4]

$$A_{m}(\alpha)=\int_{1}^{\infty}\exp[-\alpha\lambda]\lambda^{m}\mathrm{d}\lambda, \tag{B11}$$

and

$$B_{j}(\beta)=\int_{-1}^{1}\exp[-\beta\mu]\mu^{j}\mathrm{d}\mu. \tag{B12}$$