Analytical functions for the calculation of hyperspherical potential curves of atomic systems

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The Hyperspherical Adiabatic Approach (HAA) [1, 2, 3] is an adequate method to treat N-body systems interacting with the long-range Coulombian forces due to its molecular-like description using potential curves that bring us to mind the spirit of the Born-Oppenheimer approximation. For two electron atomic systems (N=3) the HS coordinates are, $R^2 = r_1^2 + r_2^2$, $\tan\alpha = r_1/r_2$. With those coordinates the hyperspherical Schrödinger equation has the compact form

$$\left[\frac{d^2}{dR^2} - \frac{\hat{U}(R;\Omega) - 1/4}{R^2} + \varepsilon\right](\sin\alpha\cos\alpha R^{5/2}\psi(R,\Omega)) = 0, \tag{1}$$

where ε is the system energy and the operator $\hat{U}(R;\Omega)$ depends on all compact variables $\Omega = (\alpha, \phi_i, \theta_i; i = 1,2)$ and on the hyper-radius R through the expression

$$\hat{U} = C_2\left(O(3N-3)\right) + R\hat{V}(R;\Omega), \tag{2}$$

where C_2 is the Casimir operator of the $O(3N-3)$ group and $\hat{V}$ is the interparticle potential energy. The eigenstates of $\hat{U}$ are the channel functions, $\Phi_\lambda(R;\Omega)$ with eigenvalues forming potential curves $U_\lambda(R)$ as function of R. In the Hyperspherical Adiabatic Approach (HAA) the total wave function is expanded in the basis formed by the channel functions,

$$\psi(R,\Omega) = \sum_\lambda F_\lambda(R)\Phi_\lambda(R;\Omega), \tag{3}$$

which leads to a set of coupled equations for the radial components $F_\lambda(R)$.

By introducing the variable $z = \tan(\alpha/2)$ [2, 4] we present a fast convergent analytical angular basis functions to expand $\Phi_\lambda(R;\Omega)$ which generalizes the Jacobi polynomials. We show that these functions, obtained by selecting the diagonal terms of the angular equation with respect to the total angular momentum function $\mathcal{Y}^{LM}_{\ell_1\ell_2}(\hat{r}_1,\hat{r}_2)$, allow efficient diagonalization of the Hamiltonian for all values of the hyperspherical radius [5].

For the Li^+ ion and helium atom with $L = 0$ and total spin $S = 0$ the ground state energy obtained as a function of the number of radial coupled components are given on table I.

Table 1: Ground state energy of the Li^+ as a function of the number of coupled radial equations.

N_c	Li^+ Energy (a.u.)	Error (ppm)	He Energy (a.u.)	Error
1	−7.262 640 06	2 372.737	−2.895 553 56	2 813.911
3	−7.279 704 90	28.639	−2.903 611 47	38.882
7	−7.279 897 74	2.149	−2.903 717 07	2.515
13	−7.279 909 25	0.568	−2.903 723 00	0.475
21	−7.279 910 83	0.351		

The method also allows the calculation of excited states when the correct radial assymptotic condition is considered [6]. Some results are shown on Table II.

Table 2: Lowest binding energies of the Li^+ [5] and Helium [7]

State	Li^+ Energy (a.u.)	Error (ppm)	He Energy (a.u.)	Error (ppm)
1s1s	−7.279 910 8	0.35	−2.903 723 00	0.48
1s2s	−5.040 865 9	2.15	−2.145 956 96	7.96
1s3s	−4.733 725 0	6.44	−2.061 242 87	14.13
1s4s	−4.629 749 1	7.15	−2.033 567 78	9.31
1s5s	−4.582 401 5	5.64	−2.021 164 76	5.98

Acknowledgments.

This work was supported by the agencies CNPq and FAPESP (proc. 98/03044-7 and 97/06271-1).

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