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Hyperspherical angular adiabatic separation for three-electron atomic systems

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The hypothesis of treating three-electron systems as a two-electron core plus a bound electron in the hyperspherical adiabatic approach introduces a second adiabatic separation into hyperangular equations. Differently from the main radial-angular hyperspherical adiabatic separation, the resulting couplings are necessary to guarantee permutational and rotational invariance of the Hamiltonian. Thus, any kind of approximation, disregarding such couplings, represents a loss of symmetry. This paper explores the consequences of such approximations in the potential curve calculations for the lithium atom, showing that this symmetry breaking is quite smooth and can be recovered within a good precision adding few couplings to the system of angular differential equations.

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The hyperspherical adiabatic approach (HAA), developed in atomic physics by Macek [1], Fano [2], and Lin [3], describes the system in terms of "molecularlike" potential curves, derived from the adiabatic separation of the radial and angular parts of Schrödinger equation in hyperspherical coordinates. Resonance positions of helium, associated to the doubly excited states, potential curve calculations, and analysis of the two-electron correlations were performed by Macek [1] and Lin [4], and numerically stable results have made possible the nonadiabatic calculations, establishing highly accurate results for the two-electron atoms [5–10]. The three-electron system has been analyzed in the HAA, since the 1980s [11,12]. New theoretical techniques have been applied for solving the three-electron adiabatic eigenvalue problem in direct numerical schemes [13–17]. Potential curves and channel functions were obtained focusing on the correlation properties of the doubly and triply excited states of the three-electron atoms [18], showing that the HAA provides an elegant and conceptually clear description of such systems. However, the extension of the HAA calculation to three-electron systems has not reached the success achieved for the two-electron system, preventing a quantitative investigation. Consequently, the power and merit of the hyperspherical approach are partially lost for such systems.

The potential curves and channel functions for two-electron atoms are solutions of a coupled system of ordinary differential equations in the hyperangle α, which is related to the relative distances from the electrons to the nucleus. In the HAA, the inclusion of one more electron fundamentally changes the hyperangular equations by the inclusion of one more hyperangle β and the potential curve calculations will involve solutions of a coupled system of partial differential equations in both hyperangles α and β. Numerically this problem is much more complicated than the analogous one for the two-electron atoms. Due to the energy dominant aspect of the two-electron core in three-electron atoms (the ground-state energy of the Li^+ ion represents 97% of the ground-state energy of the Li atom), the two-electron channel functions have been used here as a basis for the hyperangular solutions. This choice produces a second (angular) adiabatic separation between the innermost hyperangle α and the outermost hyperangle β, transforming the problem of a system of partial differential equations into the problem of two coupled systems of ordinary differential equations. A first study of the angular adiabatic separation was done in Ref. [17]. The present work provides a complete description of the principal features and consequences of this approach.

Since the hyperradius R is invariant under any electron permutation and under O(9) rotational transformations, all symmetry properties are located in the angular equations. The second angular adiabatic separation introduces (angular and radial dependent) nonadiabatic couplings as well as couplings due to the electron correlation between the outermost and the two innermost electrons. These couplings are not invariant under the above-mentioned symmetry operations. Thus, the adiabatic approximation, disregarding the off-diagonal couplings in the angular equations, induces a loss of invariance of the Hamiltonian in both permutational and rotational aspects. This paper investigates the consequences of this kind of approximation in a model problem considering just the electron-nucleus interactions. This model gives an opportunity to analyze the convergence of the potential curves when the nonadiabatic couplings are systematically introduced, without worrying about the convergence related to the electron-electron couplings and allowing the learning of an important aspect of the angular adiabatic separation, which must be considered for further precise description of the three-electron problem.

The hyperspherical coordinates for a three-electron system are obtained replacing the electronic radial distances r_1, r_2, and r_3, by a hyperradius R and two hyperangles α and β defined by $r_1 = R\sin\beta\sin\alpha$, $r_2 = R\sin\beta\cos\alpha$, and $r_3 = R\cos\beta$, with $0\leqslant R<\infty$, $0\leqslant\alpha\leqslant\pi/2$, and $0\leqslant\beta\leqslant\pi/2$. The spherical angles are kept unchanged.

In the HAA, the total wave function results from the adiabatic separation of the angular and radial variable, expanded in terms of the channel function basis $\Phi_\lambda(R,\Omega)$,

$$\Psi(R,\Omega)=\sum_{\lambda} J_\lambda(R)\Phi_\lambda(R,\Omega), \tag{1}$$

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*Electronic address: jpdincao@if.sc.usp.br where Ω is the set of all angles and λ is the channel index. The channel functions $\Phi_\lambda(R,\Omega)$ are the eigenfunctions of the angular equation

$$\hat{U}(R,\Omega)\Phi_\lambda(R,\Omega)=U_\lambda(R)\Phi_\lambda(R,\Omega), \tag{2}$$

with eigenvalues given by the potential curves $U_\lambda(R)$ obtained for fixed values of R. The radial dependence of the channel functions leads to an invariant set of coupled radial equations

$$\left(\frac{d^2}{dR^2}+\frac{U_\lambda(R)+1/4}{R^2}+2E\right)J_\lambda(R) + \sum_{\lambda'}\left(2P_{\lambda\lambda'}(R)\frac{d}{dR}+Q_{\lambda\lambda'}(R)\right)J_{\lambda'}(R)=0, \tag{3}$$

where $P_{\lambda\lambda'}(R)$ and $Q_{\lambda\lambda'}(R)$ are the nonadiabatic couplings [19,20]. The hyperangular potential operator

$$\hat{U}(R,\Omega)=\frac{\partial^2}{\partial\beta^2}+\frac{\hat{u}(\rho,\overline{\Omega})+1/4}{\sin^2\beta}-\frac{\hat{L}_3^2}{\cos^2\beta}+\frac{2RZ}{\cos\beta} +2R\hat{C}_{[ee]}(\Omega) \tag{4}$$

contains the potential operator of the two-electron core given by

$$\hat{u}(\rho,\overline{\Omega})=\frac{\partial^2}{\partial\alpha^2}-\frac{\hat{L}_1^2}{\sin^2\alpha}-\frac{\hat{L}_2^2}{\cos^2\alpha}+\frac{2\rho Z}{\sin\alpha}+\frac{2\rho Z}{\cos\alpha} +2\rho\hat{\mathcal{C}}_{[ee]}(\overline{\Omega}), \tag{5}$$

where $\rho=R\sin\beta=(r_1^2+r_2^2)^{1/2}$ and $\overline{\Omega}$ are, respectively, the two-electron hyperradius and the set of angles related to the core variables; $\hat{\mathcal{C}}_{[ee]}$ represents the electron correlation of the two innermost electrons and $\hat{C}_{[ee]}$ represents the correlation between the outermost and the two innermost electrons. Each $\hat{L}_i$ is the individual angular-momentum operator of the electronic motion. Thus, it is possible to establish an angular adiabatic separation expanding the total channel function in terms of the two-electron channel functions ϕ_γ, i.e.,

$$\Phi_\lambda(R,\Omega)=\sum_\gamma F_\gamma^\lambda(R,\beta)\phi_\gamma(\rho,\overline{\Omega}), \tag{6}$$

where γ represents a set of quantum numbers. The two-electron channel functions form a complete set of orthonormal functions determined by the solution of the two-electron potential equation for fixed values of ρ,

$$\hat{u}(\rho,\overline{\Omega})\phi_\gamma(\rho,\overline{\Omega})=u_\gamma(\rho)\phi_\gamma(\rho,\overline{\Omega}), \tag{7}$$

where $u_\gamma(\rho)$ is the two-electron core potential curve. Therefore, this second adiabatic separation makes possible to analyze the whole problem in a different systematic, considering the motion of the two innermost electrons and the outermost electron separately. First of all, it is necessary to establish the solutions of the two-electron problem to analyze the solutions of the three-electron potential equation in terms of the core potential curves.

Traditionally, the two-electron channel functions, i.e., solutions of Eq. (7), are expanded in terms of the generalized spherical harmonics for two individual angular momenta. In the present study, the two-electron channel functions have to be eigenfunctions with total angular momentum L, including the angular momentum of the third electron to form such state. Therefore, the channel functions are expanded in terms of the generalized spherical harmonics $\mathcal{Y}^{LM}_{l_1l_2(l_{12})l_3}$ for three individual angular momenta

$$\phi_\gamma(\rho,\overline{\Omega})=\sum_{l_1l_2}G^{(\gamma)}_{l_1l_2}(\rho,\alpha)\mathcal{Y}^{LM}_{l_1l_2(l_{12})l_3}(\Omega_1,\Omega_2,\Omega_3), \tag{8}$$

where the Ω_i's are the spherical angles and γ labels the solutions $G^{(\gamma)}_{l_1l_2}$ of the coupled system of ordinary differential equations deduced by applying Eq. (8) in Eq. (7) leading to

$$\left(\frac{\partial^2}{\partial\alpha^2}-\frac{l_1(l_1+1)}{\sin^2\alpha}-\frac{l_2(l_2+1)}{\cos^2\alpha}+\frac{2\rho Z}{\sin\alpha}+\frac{2\rho Z}{\cos\alpha}-u_\gamma(\rho)\right) \times G^{(\gamma)}_{l_1l_2}(\rho,\alpha)=-2\rho\sum_{l_1'l_2'}\mathcal{C}^{l_1l_2}_{l_1'l_2'}(\alpha)G^{(\gamma)}_{l_1'l_2'}(\rho,\alpha), \tag{9}$$

where the couplings $\mathcal{C}^{l_1l_2}_{l_1'l_2'}(\alpha)$ are due to the electronic correlation given by the spherical harmonic expansion. In the electron-nucleus model the above equation is diagonal and the two-electron potential curves can be determined by imposing the vanishing of the solution or its first derivative at $\alpha=\pi/4$, for the triplet and singlet symmetries, respectively [19].

The functions F^λ_γ, from the angular adiabatic separation [Eq. (6)], are solutions of the set of coupled differential system deduced from the orthogonality relations of the two-electron channel functions

$$\left(\frac{\partial^2}{\partial\beta^2}+\frac{u_\gamma(\rho)+1/4}{\sin^2\beta}-\frac{l_3(l_3+1)}{\cos^2\beta}+\frac{2RZ}{\cos\beta}-U_\lambda(R)\right)F^\lambda_\gamma(R,\beta) =-\sum_{\gamma'}\mathcal{W}_{\gamma\gamma'}(R,\beta)F^\lambda_{\gamma'}(R,\beta). \tag{10}$$

Differently from the two-electron angular problem, two kinds of couplings have been found in $\mathcal{W}_{\gamma\gamma'}$. One of them $C_{\gamma\gamma'}$ is the Coulombian coupling of the outermost electron with the innermost ones, and the other is the nonadiabatic couplings, $p_{\gamma\gamma'}$ and $q_{\gamma\gamma'}$, due to the basis dependence on the coordinate β. Then, $\mathcal{W}_{\gamma\gamma'}$ is given by

$$\mathcal{W}_{\gamma\gamma'}(R,\beta)=-2R\,C_{\gamma\gamma'}(R,\beta)+2p_{\gamma\gamma'}(\rho)\frac{\partial}{\partial\beta}+q_{\gamma\gamma'}(\rho), \tag{11}$$

where

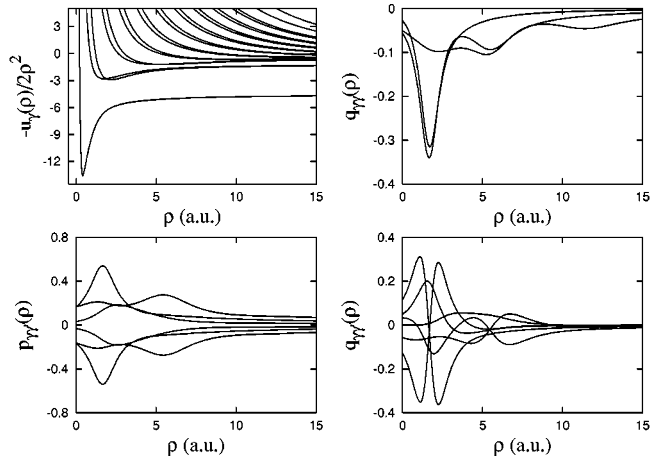

FIG. 1. Potential curves and nonadiabatic couplings for the $^1S^e$ Li$^+$ ion. The nonadiabatic terms were calculated using a five point, second-order differentiation formula and a Gauss-Legendre integration [21].

$$p_{\gamma\gamma'}(\rho)=\left\langle \phi_\gamma \middle| \frac{\partial}{\partial\beta} \middle| \phi_{\gamma'} \right\rangle, \tag{12}$$

$$q_{\gamma\gamma'}(\rho)=\left\langle \phi_\gamma \middle| \frac{\partial^2}{\partial\beta^2} \middle| \phi_{\gamma'} \right\rangle, \tag{13}$$

where the integration is done over the spherical angles and the hyperangle α. Disregarding the electronic correlations, the only couplings are the angular nonadiabatic terms. A set of two-electron potential curves and nonadiabatic couplings, used in our three-electron potential curve calculations, are shown in Fig. 1. The comparison between the two-electron potential curves and the nonadiabatic couplings in Fig. 1, indicate that the coupling terms of Eq. (10) are sufficiently small and a good convergence is therefore expected. The three-electron potential curves are determined establishing the matching of all $F_\gamma(R,\beta)$ components and their first derivative simultaneously at $\beta=\pi/4$, i.e., the propagated solutions of Eq. (10) and their first derivative from $\beta=0$ have to match the solutions propagated from $\beta=\pi/2$, at $\beta=\pi/4$. Since the matching condition does not take into account any symmetry property, it is natural that some solutions do not pertain to the doublet and quartet symmetries of the lithium atom and have to be excluded. In Ref. [17] a set of approximated boundary conditions was proposed in order to determine the potential curves for the three-electron systems. However, this set of approximated boundary condition led to a qualitative investigation for both potential curves and channel functions, since accurated physical solutions require exact boundary conditions. In the present calculation, the unique approximation refer to the number of couplings considered in the Eqs. (9) and (10). Potential curves for the lithium atom in the diagonal approximation, including only the diagonal term $q_{\gamma\gamma}(\rho)$, are shown in Fig. 2 for both doublet and quartet symmetries in a s^3 and sp^2 angular-momentum configuration.

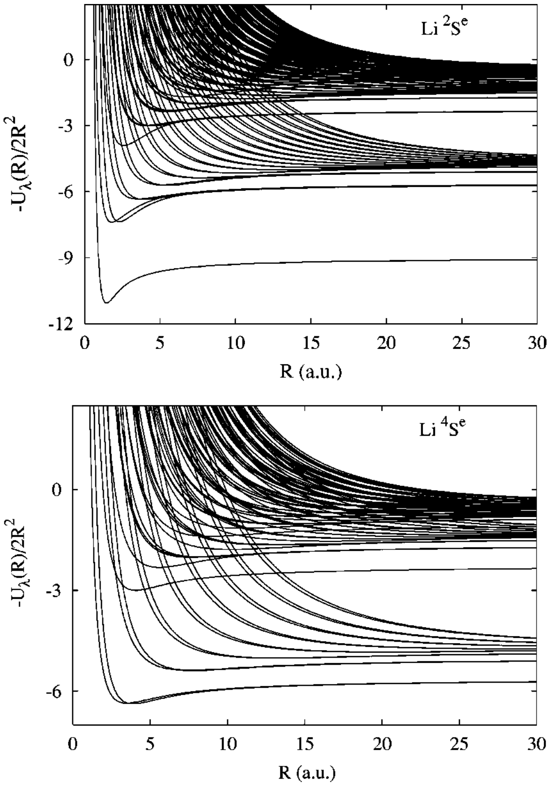

FIG. 2. Potential curves for the Li atom, for the doublet and quartet symmetries, calculated using the triplet two-electron potential curves.

The main idea of the present study derives from the observation that for the doublet symmetry potential curves, a particular kind of degeneracy is expected. The channel functions for such symmetry have two components; one is a singlet and the other is a triplet parent of the associated two-electron channel functions, combined to give an antisymmetric total wave function

$$\Phi_\lambda(R,\Omega)=\chi^{(0)}\Phi_\lambda^{(0)}(R,\Omega)-\chi^{(1)}\Phi_\lambda^{(1)}(R,\Omega), \tag{14}$$

where $\chi^{(s)}$ the is total spin eigenstate $S=1/2$ components with intermediate spin $s=0$ (singlet) and $s=1$ (triplet). Due to the invariance of the potential-energy operator [Eq. (4)] with respect to the spin, some of the three-electron potential curves calculated using singlet and triplet potential curves are expected to show the pattern of degeneracy $U_\lambda(R)=U_\lambda^{(0)}(R)=U_\lambda^{(1)}(R)$, associated with the doublet potential curves. Since the coupling terms of Eq. (10) depend essentially on the two-electron hyperradius ρ, they are invariant under permutation of the innermost electrons and O(6) rotational transformations in the absence of the electronic correlation. However, they are not invariant under the three-electron permutation group and the overall rotation group O(9) individually, and the invariance of the Hamiltonian is only reached considering all coupling terms. In this sense, the angular adiabatic approximation keeps the innermost symmetries but does not preserve the overall invariance. Since degeneracy in quantum mechanics is related to the existence of groups of symmetry under which the Hamiltonian is invariant, the angular adiabatic approximation artificially removes the above required degeneracy for the doublet potential curves, causing a symmetry breaking. Thus, a nonadiabatic angular calculation, i.e., introducing the off-diagonal couplings, not only corrects the adiabatic separation features but also recovers the invariance of the Hamiltonian and the above-mentioned degeneracy.

In order to recover the invariance of the Hamiltonian, the convergence of the three-electron potential curves is analyzed when the nonadiabatic couplings are introduced. The difference $\Delta U_\lambda(R) = |U_\lambda^{(0)}(R) - U_\lambda^{(1)}(R)|/(2R^2)$, between the singlet and triplet parents, gives a measure of the degeneracy between the doublet potential curves, since it is expected that $U_\lambda^{(0)}(R) = U_\lambda^{(1)}(R)$, for an exact calculation. As shown at Fig. 3, the degeneracy is recovered with good accuracy when the coupling terms are included. This result points out the accuracy of the potential curves calculated by solving Eq. (10), recovering the expected degeneracy.

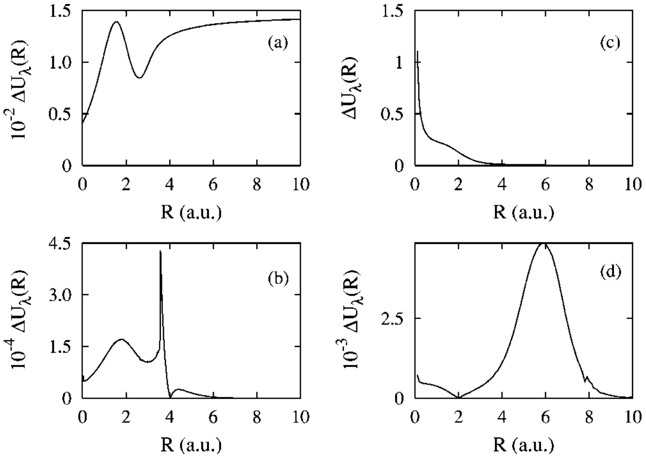

FIG. 3. Difference $\Delta U_\lambda(R)$ for the lowest potential curve calculated with one channel and two coupled channels, (a) and (b), respectively, and for the second lowest potential curve with one and two coupled channels, (c) and (d), respectively.

In conclusion, the above results show that the symmetry breaking introduced by the adiabatic approximation is quite smooth and the total invariance can be recovered when few couplings are introduced, which is reflected by the doublet potential curve degeneracy. Thus, the method can be pointed out as an alternative procedure to analyze the three-electron problem using two systems of ordinary differential equations instead of solving partial differential equations. Only few couplings need to be introduced to achieve good accuracy. Moreover, the angular adiabatic separation makes possible to calculate several potential curves supporting doubly and triply excited states in the adiabatic approximation with a very fast and precise numerical approach. This is the subject for future investigation.

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[1] J.H. Macek, J. Phys. B **1**, 831 (1968).
[2] U. Fano and C.D. Lin, *Atomic Physics* (Plenum, New York, 1975), Vol. 4, p. 47; U. Fano, Rep. Prog. Phys. **46**, 97 (1983).
[3] C.D. Lin, Phys. Rev. A **10**, 1986 (1975); **12**, 493 (1975); **14**, 30 (1976).
[4] C.D. Lin, Phys. Rev. A **23**, 1585 (1981); **25**, 76 (1982); **26**, 2305 (1982); Phys. Rep. **257**, 1 (1995).
[5] A.G. Abrashkevich, D.G. Abrashkevich, M.I. Gaysak, V.I. Lendyel, I.V. Puzynin, and S.I. Vinitsky, Phys. Lett. A **152**, 467 (1991).
[6] A.G. Abrashkevich and M. Shapiro, Phys. Rev. A **50**, 1205 (1994).
[7] O.I. Tolstikhin, S. Watanabe, and M. Matsuzawa, Phys. Rev. Lett. **74**, 3573 (1995).
[8] M. Masili, J.E. Hornos, and J.J. De Groote, Phys. Rev. A **52**, 3362 (1995).
[9] J.J. De Groote, M. Masili, and J.E. Hornos, J. Phys. B **31**, 4755 (1998).
[10] J.J. De Groote, M. Masili, and J.E. Hornos, Phys. Rev. A **62**, 032508 (2000).
[11] C.W. Clark and C.H. Greene, Phys. Rev. A **21**, 1786 (1980).
[12] C.H. Greene and C.W. Clark, Phys. Rev. A **30**, 2161 (1984).
[13] C.G. Bao and C.D. Lin, Few-Body Syst. **16**, 47 (1994).
[14] X. Yang, J. Xi, C.G. Bao, and C.D. Lin, Phys. Rev. A **52**, 2029 (1995).
[15] X. Yang, C.G. Bao, and C.D. Lin, Phys. Rev. A **53**, 3934 (1996).
[16] T. Morishita and C.D. Lin, Phys. Rev. A **57**, 4268 (1998).
[17] T. Morishita, O.I. Tolstikhin, S. Watanabe, and M. Matsuzawa, Phys. Rev. A **56**, 3559 (1997).
[18] C.G. Bao, X. Yang, and C.D. Lin, Phys. Rev. A **55**, 4168 (1997); T. Morishita, Y. Li, and C.D. Lin, *ibid.* **58**, 4214 (1998); T. Morishita and C.D. Lin, *ibid.* **59**, 1835 (1999); J. Phys. B **34**, L105 (2001).
[19] J.E. Hornos, S.W. MacDowell, and C.D. Caldwell, Phys. Rev. A **33**, 2212 (1986).
[20] H.R. Sadeghpour, Phys. Rev. A **43**, 5821 (1991).
[21] *Handbook of Mathematical Functions*, 3rd ed., edited by M. Abramowitz and I.A. Stegun (Dover, New York, 1965).