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Accurate Computation of Resonant States of Three-Electron Atomic Systems: A Complex Scaled Hylleraas CI Method

Juan Carlos Cardona [a], Luis Sanz-Vicari [a], Eva Lindroth [b]

[a] Instituto de Física. Universidad de Antioquia. Medellín, Colombia.
[b] AtomPhysik, Stockholm University, Sweden.

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Resumen

Los estados doble y triplemente excitados de sistemas trielectrónicos, constituyen un problema coulombiano de cuatro cuerpos, el cual es altamente correlacionado. Para su tratamiento hemos desarrollado un programa de Interacción de Configuraciones (CI) basado en funciones de Hylleraas (Hy), para momento angular y de espín arbitrarios. El cómputo de resonancias se ha implementado mediante un escalado complejo uniforme (UCS). Nuestro código nos permite calcular estados resonantes del ion negativo del Helio con la mayor precisión posible.

***Palabras Clave*:** Coordenadas correlacionadas, Estados resonantes

Abstract

Doubly and triply excited states of three-electron systems provide the case for a highly correlated four-body Coulomb problem. We have developed a sophisticated three-electron Configuration Interaction (CI) code based on explicitely correlated Hylleraas (Hy) functions for arbitrary total angular momentum and spin, which has been implemented with an uniform complex scaling (UCS) method to deal with resonant states. At present, this UCS-HyCI tool allows us to perform computations to uncover resonant states of the Helium negative ion, with the highest accuracy possible.

***Keywords*:** Correlated coordinates, Resonant states

To deal with many-electron atomic systems, several approaches have been developed through the years. Among them, the Configuration Interaction (CI) method is the most powerful method known for the accurate calculation of atomic structure. The standard or classical CI method provides a technique to calculate approximate (but accurate) variational energies, and also many-electron wavefunctions in terms of antisymmetric products of one-electron hydrogenic wavefunctions or any other form of one-electron functions. The use of one-electron functions of central symmetry as basis set and the well-known expansion of the electron-electron repulsion potential in spherical harmonics

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} \sum_{m=-l}^{+l} \mathcal{Y}_{lm}^*(\mathbf{r}_i)\mathcal{Y}_{lm}(\mathbf{r}_j), \qquad (1)$$

notably simplifies the calculations, since the radial and angular parts are evaluated separately. Nevertheless, the rate of convergence of the classical CI method is rather slow, both with radial and angular systematic additions. Anyway we must note that the classical CI method is *exact* in nature provided we include a full set of configurations.

Being so, the limitations come from practical issues. For example, recent computations for a three-electron negative ion like He^- [1], where electron correlation effects dominate, show that in order to obtain accurate eigenenergies and eigenfunctions, one must reach up to ~ 10000 configurations in a typical CI approach. The way to overcome such difficulty is to modify the CI method to accelerate the convergence. For instance, we may abandon the advantages of using basis functions of central symmetry and to adopt correlated configuration basis functions (it means that the radial function

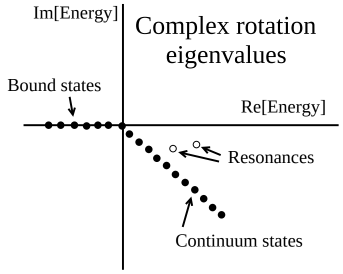

Figura 1. The complex rotation method uncovers the resonant states while continuum states rotates 2θ into the lower half of the complex plane.

explicitely contains the terms r_{ij}). This is the approach we follow in this work, to be applied to a three-electron atomic system like He$^-$ ion.
Hylleraas CI Method:

In our approach each configuration of the variational basis set contains radial, angular and spin parts, as follows:

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \mathcal{A}Rr_1, r_2, r_3, r_{12}, r_{23}, r_{31}) \, \mathrm{Y}^{LM_L}_{(\ell_1,\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\chi^{S,M_S}(1,2,3) \quad (2)$$

where the radial part consist of:

$$R(r_1,r_2,r_3,r_{12},r_{23},r_{31}) = r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}\mathrm{e}^{-\alpha r_1-\beta r_2-\gamma r_3} \quad (3)$$

and the angular part

$$\mathrm{Y}^{LM_L}_{(\ell_1,\ell_2)\ell_{12},\ell_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3) = \sum_{\text{all } m_i}\langle \ell_1 m_1;\ell_2 m_2|\ell_1\ell_2;\ell_{12}m_{12}\rangle \times \langle \ell_{12}m_{12};\ell_3 m_3|\ell_{12}\ell_3;LM_L\rangle \, \mathcal{Y}_{\ell_1 m_1}(\hat{\mathbf{r}}_1)\mathcal{Y}_{\ell_2 m_2}(\hat{\mathbf{r}}_2)\mathcal{Y}_{\ell_3 m_3}(\hat{\mathbf{r}}_3) \quad (4)$$

is a vector-coupled spherical harmonics product representing a final state of definite total angular momentum L and projection M_L. The correlated terms r_{ij}, are defined as the norms of the vectors: $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ for i,j taking cyclically values into the $\{1,2,3\}$ set. $\chi(1,2,3)$ is the spin part of the wavefunction, and $\mathcal{A}$ is the antisymmetrizer for three particles.

The major difficulty that one faces when all powers $r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}$ are present in the basis set is the evaluation of the radial integrals involved, which become much more complicate than in the classical CI method.

$$I = \int r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}e^{-\alpha r_1}e^{-\beta r_2}e^{-\gamma r_3}d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (5)$$

A method to solve the integral (5) has been introduced by Z.-C. Yan and G.W.F. Drake [2]. A full 'ab initio' computational code in C/C++ has been implemented in our group to compute Hylleraas CI eigenvalues and eigenfunctions for arbitrary total angular momentum and spin symmetries [3].

Computation of resonances: uniform complex scaling (UCS)

In order to compute resonances, we make use of a complex scaling method. When $r \to re^{i\theta}$, the Hamiltonian becomes an operator rotated in the complex plane as:

$$H(\theta) = Te^{-i2\theta} + Ve^{-i\theta} \quad (6)$$

and we diagonalize the resulting complex non-hermitian (but symmetric) matrix with standard LAPACK algebra packages. Such UCS technique uncovers resonant states as schematized in Figure 1. The uncovered resonance is a S-matrix pole in the complex plane with energy given by

$$E = E_r - i\frac{\Gamma_r}{2} \quad (7)$$

where E_r is the resonance position and Γ_r is the resonance width. They are found by closely inspecting the stabilization path of the resonance with the rotation angle (see Figure 2).

Results and conclusion.

We present computations for the ${}^4P^e$ symmetry of He$^-$ negative ion. We compare our Hylleraas CI results with those obtained with a classical CI approach using a B-splines basis set [1]. In the classical CI case, we include 9279 configurations to achieve converged results, including configurations built up with s,p,d,f and g one-electron orbitals (i.e., 3078 *spp*, 2907 *sdd*, 171 sff, 171 *sgg*, 2304 *ppd* and 648 *pdf*). In this approach we obtain the resonant parameters

$$E_r = -2{,}06507\ a.u.,\ \Gamma_r = 0{,}00142\ a.u., \quad (8)$$

for the first ${}^4P^e$ $1s3p^2$ Feshbach resonance of the He$^-$ system. The complex rotated eigenvalue spectrum is shown in Figure 2 (a). At variance, in the present Hyller-

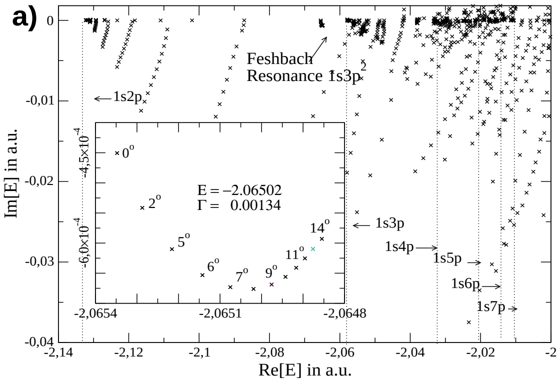

Figura 2. He^{-} $^4P^e$ complex eigenvalue spectrum computed with a) Hylleraas CI. b) classical CI. In the insets, the stabilization of the resonance location by varing the rotation angle θ is shown. Resonance parameters are taken where $\partial E/\partial\theta$ approaches a minimum.

aas CI computation, we have included *only* 378 correlated configurations of the spp angular type. The radial part of the basis in Eq. (3) is a simple product of Slater type orbitals ($e^{-\alpha r}$ for the s states and $re^{-\beta r}$ for p states). The correlation powers j_{12} and j_{23} run from 0 to 3. Nonlinear parameters α and β for 6 s and 11 p states, respectively, are generated by an even tempered geometrical sequence, i.e., exponents are built up with a series $\alpha_i = \alpha_0\xi^i$, with $i = 1\ldots 6$ and $\alpha_0 = 2$ for s states and $\beta_i = \beta_0\xi^i$ with $i = 1\ldots 11$ and $\beta_0 = 0{,}5$ for p states. A factor $\xi = 1{,}2$ ensures to complete the configurational space with diffuse states and avoids many linear dependencies in the basis set. Remaining redundancies in the basis set are eliminated before the Hamiltonian is diagonalized, by removing from the basis set those states related to eigenvalues near to zero of the overlap matrix. The resonance parameters obtained with the Hylleraas CI method are (see Figure 2(b)):

$$E_r = -2{,}06502\ a.u.,\ \Gamma_r = 0{,}00134\ a.u., \tag{9}$$

that compare rather well with (8) and it clearly shows the advantage of using correlated configurations. In conclusion, we have reached comparable results between classical CI and Hylleraas CI not only with a much reduced size of the Hamiltonian to be diagonalized but also within the spp symmetry only. We remark that radial correlated coordinates r_{ij} contribute also to accelerate the angular correlation, at variance with the classical CI. Our Hylleraas computation may be also compared with results presented by Bylicki [4]. Further work is now in progress to obtain resonant states at higher energies and to be able to compute photoionization cross section with the Hylleraas CI method.

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