

DOUBLY EXCITED STATES OF He IN A DC FIELD

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Abstract. The effects of strong electric fields on the doubly excited states of He are investigated. Strong electric-field strengths up to $F=0.02$ a.u. are used in the present study. Intrashell doubly excited states are chosen as prototype states for studying these effects. The solution of the Complex Eigenvalue Schrödinger equation is obtained using an appropriate partitioning of the wave-function and the complex rotation method. Energy shifts and field induced widths, as a function of the external field strength, are presented and analyzed.

1. INTRODUCTION

The effects of electric fields on ground or low-lying states of atoms and molecules have been studied for many years (Ryde 1976). Likewise, the doubly excited states of H^- are particularly sensitive to external electric fields and the DC-field effects on these states have been studied fairly well (Halka 2006). The effects of electric fields on the doubly excited states of He have only recently been considered by experiments (Harries et al. 2003, Halka 2006). Some recent advances in the experimental methods have given us the opportunity to study the energy shift and the field induced width of the doubly excited states of He and the modifications appearing in the photoionization cross section. The calculation of these properties and of the profile shapes is a testing case for the advanced many-body theories. The problem is more difficult than the calculation of the tunneling rates in effective one-electron systems. The semi classical theory is useful for, essentially, hydrogen-like states, whereas for a more complicated system, the formulation suggested by Fisher, Maron and Pitaevskii (1998) could be applied. A thorough and effective approach is required far from the semi-classical limit. A first principles approach, in the context of density functional approach, has been proposed by Otsuka et al. (2004), but applications on non-stationary states are not reported.

The *ab initio* theoretical approach introduced by Themelis and Nicolaides (2000, 2001) is the background for the recent study. A general and computationally feasible theoretical approach has been developed for the study of the Stark effect on many electron atomic systems, in both ground and in excited states. The complex coordinate rotation method is used for the solution of the Complex Eigenvalue Schrödinger Equation. The main characteristic of the present approach is the partitioning of the function space used for the description of the atomic or molecular states, with or

without the existence of an external perturbation. Application of the theory has been reported for ground or excited states and the present problem is a natural generalization.

For non-stationary states there is already a finite lifetime whereas the application of an electric field can increase or decrease it, as a function of the applied field strength. For the width of an autoionizing state in a DC field we can write:

$$\Gamma(F) = \Gamma_{aut} + \Gamma_{DC}(F). \quad (1)$$

Γ_{aut} is the autoionization width and the problem here is actually the determination of the field induced width, $\Gamma_{DC}(F)$. For a bound state the usual dependence of the field-induced width on the field strength F is $\Gamma_{DC}(F) \sim e^{-k/F}$, where k is a parameter depending on the ionization potential, the angular momentum of the escaping electron etc. We will see that this rule does not apply in the case of the doubly excited states (DES) of He. An old suggestion made by Khomskii (1965) and reinvented by Davis and Jacobs (1975), brings forth a dependence of Γ_{DC} on F^2 and describes fairly well the exact values of the width in a large interval of values of F .

2. THEORY AND METHODOLOGY

The calculation of field-induced properties of atoms or molecules, in the present approach is formulated as a problem of solving variationally a complex eigenvalue Schrodinger equation (Kukulín et al. 1988):

$$(\hat{H} - \epsilon)\Psi = 0, \quad (2)$$

where: $\hat{H} = \hat{H}_{atom} + \sum_i \vec{r}_i \cdot \vec{F}$ and $\epsilon = E_0 + \Delta(F) - \frac{i}{2}\Gamma(F)$. H_{atom} is the free-atom Hamiltonian and \vec{F} the external dc-field. E_0 is the field-free energy of the state of interest, described by the field-free wave-function Ψ_0 , while $\Delta(F)$ and $\Gamma(F)$ are the field-dependent energy shift and width. Resonances are eigenvalues of \hat{H} with $\epsilon = \text{complex energy}$ ($\Gamma > 0$). A straightforward description of such states are difficult because their wave functions are exponentially divergent in the asymptotic region. In this method the eigenvalue problem of a transformed Hamiltonian

$$\hat{H}_\theta = \hat{U}(\theta)\hat{H}\hat{U}^{-1}(\theta) \quad (3)$$

is solved, instead of the original \hat{H} . The effect of the complex scaling transformation, in equation (3), is that the positive-energy continuum of \hat{H} gets rotated down into the complex energy plane, while the wave function of any resonance becomes square-integrable (if $0 < \theta < \pi/3$).

The trial wave-function Ψ , which will be computed by a variational procedure, is expanded in a function space that is divided into two nonorthogonal parts Q and P . The Q space, in general, contains correlated wave-functions belonging to the bound spectrum. The P space contains states that represent the multichannel continuous spectrum. These states are expanded in terms of L^2 functions, since the complex coordinate transformation $\hat{U}(\theta)$ makes them square integrable. The Stark Hamiltonian matrix which is derived from this choice of the basis functions is:

$$\mathbf{H} = \begin{pmatrix} H_{QQ} & H_{QP} \\ H_{PQ} & H_{PP} \end{pmatrix} \quad (4)$$

\mathbf{H} is diagonalized repeatedly in respect to changes of the non-linear parameters in the basis set of the space P and in the rotation angle θ , until the root having the maximum overlap with Ψ_0 is stabilized.

2. 1. APPLICATION TO DES OF HE

For the calculation of the localized part of the autoionizing states, we use a multi-configuration Hartree-Fock (MCHF) approximation. For example, the $2s2p\ ^3P^o$ state can be described accurately by a 3×3 minimal approximation to the wave-function: $\Psi(2s2p\ ^3P^o) = 0.992(2s2p) - 0.118(2p3d) + 0.049(3s3p)$. The energy that corresponds to the expectation value of $\widehat{Q}\widehat{H}\widehat{Q}$ for this wave-function is: $E_0(2s2p\ ^3P^o) = -0.760935$ a.u. For the description of the nearby lying non-relativistically bound state $2p^2\ ^3P$, we use an approximation of a similar accuracy. The energy that results from the calculation for this state is $E_0(2p^2\ ^3P) = -0.710190$ a.u. The function space Q for the manifold of the triplet-spin states is not consisted only by these two states. The states that are also included in our calculation are:

- i. the singly excited states $1sn\ell$, $n \leq 6$ and $\ell \leq n - 1$.
- ii. intershell autoionizing and bound states lying below the threshold $n=2$ of He^+ , that is $2\ell n\ell'$, $2 \leq n \leq 6$ and $\ell, \ell' \leq 5$.
- iii. higher lying double excited states of the form $n'\ell'n''\ell''$, with $3 \leq n' \leq n'' \leq 6$, lying below higher thresholds of He^+ .

Singly excited states are represented by compact but accurate MCHF expansions or by their HF functions. The doubly excited states are represented by CI expansion in a hydrogenic basis set, which proved to provide an accurate description of the localized part of these states. The symmetry of all of the above cited doubly excited states is for limited values of the total angular momentum $L \leq 4$.

All the above singly and doubly excited states are the members of the Q -space included in our calculations. However, in order to have a complete description of the field-free or non-zero field problem, we have to include the multichannel continuum described by the complementary function space P . The open channel components of the resonant wave-functions are represented as: $X(n\ell\varepsilon\ell'\ ^{2S+1}L^\pi) = \hat{A}(\phi_{n\ell}(r_1^*)u_{\varepsilon\ell'}(\vec{\rho}_2^*)) = \hat{A}(\phi_{n\ell}(r_1^*) \sum_i c_i \chi_i(\rho_2^*) Y_{\ell m}(\Omega_2))$. \hat{A} is an antisymmetrizer and $\phi_{n\ell}$ are hydrogen-line states with $Z=2$ and $u_{\varepsilon\ell'}$ are states belonging to the continuum represented as a linear combination of $\chi_i(\rho^*) = (\rho^*)^{k_i} e^{-a_i \rho^*}$. In the variant of the complex-coordinate approximation followed here, for $\chi_i(\rho^*)$ the radial coordinate takes the form $\rho_i^* = r_i e^{-i\theta}$. The non-linear parameters a_i and the expansion coefficients c_i are subject to a variational optimization for the calculation of the complex energy eigenvalues pertaining to the autoionizing and field induced resonant states.

3. RESULTS

In the case of the absence of electric field, for the triplet-spin states of interest, we have found for their energy position the following results: $E(2s2p\ ^3P^o) = -0.760150$ a.u. and $E(2p^2\ ^3P) = -0.710218$ a.u.. The energy width of the autoionizing state is: $\Gamma(2s2p\ ^3P^o) = 0.0003126$ a.u.. In Fig. (1a) we show the movement of the resonance poles for the $2s2p\ ^3P^o$ and $2p^2\ ^3P$ states ($M = 0$ and $M = \pm 1$) when the external electric field is turned on. For the field-free case, the $2s2p\ ^3P^o$ state lies at a position of ~ 0.05 a.u. lower than the $2p^2\ ^3P$ state. When the external electric field is turned

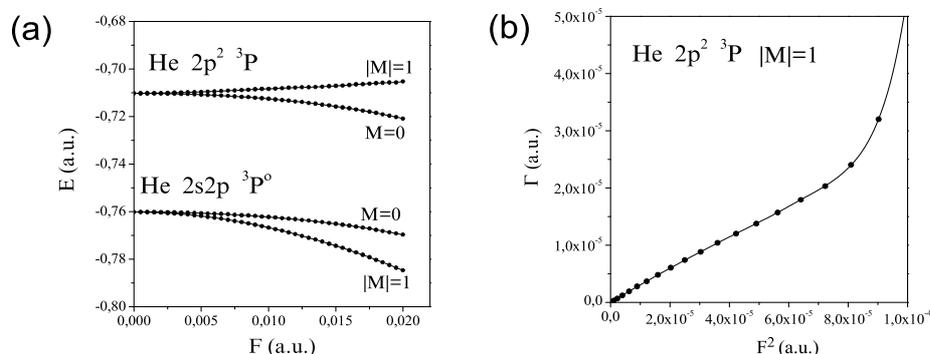


Figure 1: Energies and widths as functions of the DC-field.

on, the interaction between the two resonant poles having $M = \pm 1$ is evident, as they start to repel each other in the complex-energy plane. This is not the case for the states with $M = 0$ since, according to the selection rules for the external perturbation, they do not interact. The width for the $2s2p \ ^3P^o$ states decreases for small values of F whereas for higher values of F starts to increase. At the same time, the width for the $2p^2 \ ^3P$ state increases when the field strength is increased. In Fig. (1b) we show the change in width of the state $2p^2 \ ^3P$, $M = \pm 1$ as a function of the squared external electric-field strength F . It is clear that for low values of F the width has a linear dependence on F^2 . This dependence has been predicted many years ago by Khomskii (1965). It is further noted that when the external electric-field strength is greater than 8×10^{-5} a.u. approximately, the width for the $2p^2 \ ^3P$, $M = \pm 1$ state increases quite rapidly. At the high-field region, the effective potential barrier, formed by the combination of the atomic potential and the external DC field, would become narrower as the external electric-field strength is increased further.

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