EFFECTS OF STATIC ELECTRIC FIELDS ON DOUBLY EXCITED STATES OF He

S.I. Themelis

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, GR-711 10 Heraklion, Greece
E-mail: stheme@iesl.forth.gr

Abstract

The effects of strong electric fields on the spectrum of doubly excited states of He are investigated. The doubly excited states $2p^2\ ^3P$ and $2s2p\ ^3P^o$ are chosen as prototype states for studying these effects. The solution of the Complex Eigenvalue Schrödinger equations pertaining to these states is obtained using and appropriate partitioning of the wave function and the complex rotation method. The changes of the resonance energies and widths as a function of the external field strength are presented.

1. Introduction

Doubly excited states of atoms remain in the front of the scientific research for more than two decades. The existence and properties of these states owe much to the strong radial and angular correlation between the two excited electrons. Many theoretical approaches are used in order to study the properties and the dynamics of these states. In a recent publication [1], Kiselyov used a semi-classical approach and a model sphere atom for the description of the doubly excited states of He. Using a similar application of the semi-classical approach, Kiselyov also calculated the energies of doubly excited states of He, in an external electric field [2]. The rotating two-electron atoms in an external electric field have also been studied within the classical approach [3].

The effects of electric fields on the doubly excited states of He have recently been considered, both in theory and experiment [4, 5]. These effects on ground or low-lying states of atoms and molecules have been studied for many years [6]. Nevertheless, some recent advances in the experimental methods have given the opportunity to study the effect of electric field on the doubly excited states of He and the modifications appearing in the photoionization cross section [4]. 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 [7]. The calculation of the energy shift and the field-induced ionization rate is a testing case for the advanced many-body theories. The problem is more difficult than the calculation of the tunnelling rates of effective one-electron systems. For these states the semi classical theory of Ammosov, Delone and Krainov [8] is useful and for a more complicated system the theory of Fisher, Maron and Pitaevskii [9] could be applied. However, far from the semi-classical limit a thorough and effective approach is required. A theory form first principles have been published by Otobe *et al* [10] in the context of density functional approach, but applications on doubly excited states are not reported. The theoretical approach introduced by Themelis and Nicolaides ([11, 12] and references therein) is the background for the recent study. The complex coordinate rotation method in combination with an appropriate partitioning of the wave function is used for the solution of the Complex Eigenvalue Schrödinger Equation (CESE).

Application of the theory has been done for other systems, like ground or excited states and the application to this problem is a natural generalization.

The rest of the paper is organized as follows. In the next section we will epitomize the theoretical approach that is applicable for treating any state of an atom or a molecule in an electric field. In section 3 some details of the calculations are given and we present the results of our calculations. In the last section some conclusions are drawn. Atomic units are used throughout this paper unless otherwise stated.

2. Theory

A general and computationally feasible theoretical approach for the study of the Stark effect on many electron atomic systems in ground as well as in excited states has been developed and applied for calculating the energy shift and the width of an atom in an electric field ([11, 12] and references therein). For small values of the field strength the results of the theory are comparable to those of the ADK theory [8] (or those of Fisher et al. [9] for a more complicated case). However, these semi-classical approaches are only applicable to bound states. For non-stationary states there is already a finite lifetime and 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:

$$\Gamma(F)=\Gamma_{aut}+\Gamma_{DC}(F), \tag{1}$$

and the problem is actually the determination of $\Gamma_{DC}(F)$. 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 constant depending on the ionization potential, the angular momentum of the electron etc. We will see that this rule does not fit in the case of the bound state $2p^2\ ^3P$ of He.

The main characteristic of our 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. An overview of the followed method is described in the following.

2.1 Complex eigenvalue Schrödinger equation for Stark resonances

In the configuration interaction in the continuum theory the staring point is the standing wave superposition of a localized state Ψ_o of energy E_o with the continuum states $u(E)$. In the neighborhood of E_o the Schrödinger equation is written as:

$$\hat{H}\,\Psi(E)=E\Psi(E)\ , \tag{2}$$

where Ψ (E) is energy normalized and has the form [13, 14]:

$$\Psi(E)=\alpha(E)[\Psi_o + \wp \int \frac{V_{oE'}}{E-E'} u(E')dE' + \lambda(E) V_{oE} u(E)\,] \tag{3}$$

($\wp$=Principal value). The energy-dependent function V_{oE} is given by $V_{oE}=\langle\Psi_o|\,\hat{H}\,|u(E)\rangle$, with $\hat{H}=\hat{H}_o+\hat{U}_s$. $\hat{H}_o$ is the Coulomb Hamiltonian and $\hat{U}_s=-e\sum_i \vec{r}_i.\vec{F}$ and λ (E) is a function, to be determined by the boundary conditions. The width, Γ, and the shift, Δ, are given by:

$$\Gamma = 2\pi\left|V_{oE}\right|^2, \qquad \Delta = \wp \int \frac{\left|V_{oE'}\right|^2}{E-E'} dE' \tag{4}$$

and the total energy is given by

$$E = E_o + \Delta(E) + \lambda(E)\left|V_{oE}\right|^2 . \quad (5)$$

The physical information carried by the wave-function Ψ (E) of Eq. (3) is revealed by considering its asymptotic form, $\left\langle \vec{r} \,|\, \Psi(\mathbf{E}) \right\rangle_{\vec{r}\to\infty} = \Psi(\vec{r} \to \infty)$. The wave functions $u(E)$ determine the asymptotic form of Ψ (E) and their form depends on the Hamiltonian $\hat{H}$. Regardless of their form it can be shown that the limiting value $\Psi(\vec{r} \to \infty)$ can be represented as a sum of two parts, which are recognized as representing incoming and outgoing waves [11, 15]:

$$\Psi(\vec{r})_{\vec{r}\to\infty} \sim \pi a(E) V_{oE} \sqrt{\frac{2}{\pi k}} \left\{ \frac{1}{2}\left(1 - \frac{\lambda(E)}{i\pi}\right) e^{i\varphi_E(\vec{r})} + \frac{1}{2}\left(1 + \frac{\lambda(E)}{i\pi}\right) e^{-i\varphi_E(\vec{r})} \right\}. \quad (6)$$

The phase $\varphi_E(\vec{r})$ is an energy dependent function. For a decaying system only outgoing waves survive. This implies that the coefficient of the incoming wave in equation (6) must be zero, and this leads to the value that the function λ(E) must have on resonance:

$$\lambda(E) = -i\pi \text{ , on resonance} \quad (7)$$

In this way from the boundary conditions the resonance energy E is obtained in a transparent way resulting in the complex value:

$$E = E_o + \Delta - i\pi \left|V_{oE}\right|^2 = E_R - i\frac{\Gamma}{2} \quad (8)$$

The resonance outgoing wave is obtained from equation (6):

$$\Psi_E(\vec{r}) \sim -a(E) V_{oE} \sqrt{\frac{\pi}{2k}}\, e^{i\varphi_E(\vec{r})} \quad (9)$$

The results (8) and (9) constitute a clear picture of how from the standing wave stationary state mixture of Eq. (3) the imposition of the asymptotic boundary conditions appropriate to decaying states leads to complex eigenvalues and complex eigenfunctions of the Hamiltonian. The generalization of the above equations to the multichannel case is straightforward.

The form of the resonance wave function given by equation (9) indicates that these eigenfunctions are not square integrable and calculations in Hilbert space with the conventional Hermitian rules for the calculation of matrix elements are not allowed. A method to circumvent this problem is to apply to the asymptotic form the complex rotation $\vec{r} \to \vec{\rho} = \vec{r}e^{i\theta}$. This transformation makes the resonance eigenfunction square integrable [11, 15]. We note that the complex coordinate rotation has been applied for calculating the Stark effect in hydrogen in a trial calculation [16]. The mathematical theory for the complex rotation for Stark Hamiltonians presented by Herbst and Simon [17, 18], but the application to real systems is not easy to address.

Given that the resonance consists of two parts:

$$\Psi = \alpha\Psi_o + (1-\alpha^2)^{1/2}\chi \quad (10)$$

[See Eq. (3)], the original CESE is transformed into a non-Hermitian complex eigenvalue problem with a two-part square-integrable eigenfunction. The first part, Ψ_o, is real and the second part, χ, is complex. For an isolated autoionizing state Ψ_o can be a single configuration state but for strong mixing caused by an external field Ψ_o must be a linear superposition of

states in a multidimensional function space ***Q***. The space ***Q*** represents the spectroscopically significant discrete and autoionizing states, chosen judiciously for each system by considering electronic structure and the form of the external perturbation. Likewise, a function space ***P*** is defined and used for the calculation of χ. The function space ***P*** contains continuum configurations with optimized real as well as parametrized complex orbitals representing contributions from the multichannel scattering states. The variational optimization of the functions belonging to this space allows the fine-tuning of the concerted effect of field-induced state mixing and of electron correlation and leads to the determination of the energy width and shift of the perturbed state. The efficiency of this form for the calculation of the variational wave function of Eq. (10) has been verified for both autoionization and field-induced tunneling processes resulting in high accuracy calculation of resonance states ([11, 12, 19] and references therein).

3. Details of the calculations

Autoionization of some doubly excited states of He below the threshold n=2 of He^+, resulting in a positive ion and a free electron, is forbidden. The selection rules for autoionization require both the parity and the orbital angular momentum, in the LS coupling scheme to be unchanged. Therefore, the state $2p^2\ ^3P$ cannot be observed by electron ejection. For this reason the state, which is found in the same energy region with the autoionizing state $2s2p\ ^3P^o$, is considered as a bound state. The action of a static electric field causes the mixing of these two states, so that conditions are created that can be developed as alternative means of identification of the state $2p^2\ ^3P$. We will study here in detail the effect of the DC field on these states and the changes caused in their lifetime.

For the description of the localized part of the autoionizing state $2s2p\ ^3P^o$, we use the wave function:

$$\Psi^{(0)}(\ 2s2p\ ^3P^o) = 0.992\ 2s2p - 0.118\ 2p3d + 0.049\ 3s3p$$

This wave function is calculated by the Multi-configuration Hartree-Fock (MCHF) method. The energy obtained by this wave function is $E^{(0)}(\ 2s2p\ ^3P^o) = -0.760935$ a.u. For the description of the bound state $2p^2\ ^3P$ we use the wave function:

$$\Psi^{(0)}(2p^2\ ^3P) = 0.994\ 2p^2 - 0.073\ 2p^2 + 0.086\ 3d^2 - 0.013\ 4f^2$$

The orbital and the mixing coefficients for the wave function in this case are also calculated by the MCHF method. The energy that results from the calculation for this state is $E^{(0)}(2p^2\ ^3P) = -0.710190$ a.u. In the ***Q*** space there are also included the following:

- The singly excited states: 1s2s, 1s2p, 1s3s, 1s3p, 1s3d, 1s4s, 1s4p, 1s4d, 1s4f, 1s5s, 1s5p, 1s5d, 1s5f, 1s5g.
- Autoionizing states lying below the threshold n=2 of He^+ described by the configuration states $2\ell n\ell'\ 2 < n \le 6$ and $\ell, \ell' \le 5$.
- Intrashell and intershell autoionizing states $n'\ell n''\ell''$ with $3 \le n' \le n'' \le 6$ lying near higher thresholds of He^+.

The wave functions of the singly excited states are calculated by the Hartree-Fock method and the autoionizing states are described by linear superposition of two electron configuration states in terms of hydrogenic radial functions. The symmetry of doubly excited states that we use for the calculations is for values of the total angular momentum $^3L^\pi \le 5$.

The function space ***P*** includes configuration states that describe the continuous states $1s\varepsilon\ell\ ^3L^\pi$ for $\ell \le 5$ as well as the higher lying channels $2s\varepsilon\ell'$, $2p\varepsilon\ell''$ with $\ell', \ell'' \le 5$. The states belonging to the continuum are described by a discretization on a basis constructed by com-

plex Slater type orbitals (STO), in the form $\varphi_i(\vec{\rho}) = \rho^k e^{-\alpha\rho} Y_{\ell m}(\Omega)$. Thus for the continuous states $\varepsilon\ell$ we use eight (8) orbital with ℓ=0, eight (8) orbital with ℓ=1, six (6) orbital with ℓ=2, four (4) orbital with ℓ=3, four (4) orbital with ℓ=4 and two (2) orbital with ℓ=5. Also for the continuum states $\varepsilon\ell'$ we use four (4) orbital with ℓ=0, four (4) orbital with ℓ=1, four (4) orbital with ℓ=2, four (4) orbital with ℓ=3, three (3) orbital with ℓ=4 and two (2) orbital with ℓ=5, while for continuous $\varepsilon\ell''$ we use four (4) orbital with ℓ=0, four (4) orbital with ℓ= 1, two (2) orbital with ℓ=2, two (2) orbital with ℓ=3, two (2) orbital with ℓ=4 and two (2) orbital with ℓ=5. The symmetries of the states of the continuum that we use for the description of the space P are limited for values of the total angular momentum $^3L^\pi \leq 5$. The parameters of the complex STO's of the above sets are optimized separately for each set, while the non-orthonormality conditions between them are taken into consideration in the calculation of the eigenvalues of the Hamiltonian. The optimization is performed separately and for each value of the field strength F. The final result gives that the optimization procedure results in the same values of the metabolic parameters for all values of F. For the first set of the complex STO's the most optimal value of the exponent is α_{opt} = 1.2, while for the other two sets we obtain α'_{opt} = 0.8 and α''_{opt} = 0.9. Also, stability is observed for the changes of the angle of rotation θ to the complex plane, for values $0.10 \leq \theta \leq 0.55$.

3.1. Results

Using the above described basis set for the function spaces ***Q*** and ***P***, in the absence of the electric field, for the states of interest we obtain the following results: i) the energy for the $2s2p\ ^3P^o$ state is E_1 = -0.760150 a.u. and the width is Γ_1 = 0.0003126 a.u. ii) the energy for the $2p^2\ ^3P$ state is E_2 = -0.710218 a.u. Our results for these states are in very good agreement with other published results in the literature. It is obvious that the state $2s2p\ ^3P^o$ has a large autoionizing width, which results in a lifetime τ=77 fs. This lifetime is larger than the lifetime of the corresponding well known singlet state $2s2p\ ^1P^o$ of He which is τ' = 18 fs.

The energy difference between the states $2s2p\ ^3P^o$ and $2p^2\ ^3P$ is ~0.05 a.u., which is small enough, so that there is expected strong interaction between the states with |M|=1, due to the action of an external electric field. Note that selection rules forbid the interaction between the states with M=0. The results of our calculations for these states, for various values of the external field strength F $\neq$0.0, are given in tables 1 and 2. For all the possible values of the projection $\langle L_z \rangle$ of the total orbital momentum in the axis z, the values of the field intensity that we used for the calculations are up to 0.02 a.u. The state $2s2p\ ^3P^o$ is split in two branches with M = 0 and $\pm$1, respectively. However, these two branches do not have precisely the same behavior in the action of the electric field, as it was expected. The state with M = 0 presents negative energy shift for all the values of the field strength that we examine here, and the same is observed for the states with M = $\pm$1. However, the energy shift of the former is almost three times smaller than that of the later. The main reason for this difference is the repulsion of these states with the corresponding states $2p^2\ ^3P$, M = $\pm$1, since they interact strongly.

This strong interaction results also in the variation of the energy width of the state $2s2p\ ^3P^o$, as a function of the field strength, which is by far larger than for the state with M=0. As it appears in table 1, for values of the field strength up to F ~0.013 a.u. a reduction of the energy width of the states that originate from $2s2p\ ^3P^o$ is observed, while for larger values of the intensity of the field, their energy width presents monotonous increase. However, for the states

Table 1. The energy and the width of the states $2s2p\ ^3P^o$, M=0 and $2s2p\ ^3P^o$, |M|=1 of He, as a function of the field strength F of a static electric field.

	$2s2p\ ^3P^o$, M=0		$2s2p\ ^3P^o$, |M|=1	
F(a.u.)	E (a.u.)	Γ (a.u.)	E (a.u.)	Γ (a.u.)
0.0000	-0.760150	0.0003126	-0.760150	0.0003126
0.0005	-0.760155	0.0003126	-0.760167	0.0003125
0.0010	-0.760171	0.0003125	-0.760219	0.0003122
0.0020	-0.760233	0.0003123	-0.760425	0.000311
0.0040	-0.760483	0.0003115	-0.761242	0.000307
0.0060	-0.760903	0.000310	-0.762582	0.000301
0.0080	-0.761497	0.000308	-0.764416	0.000292
0.0100	-0.762275	0.000305	-0.766716	0.000283
0.0120	-0.763250	0.000302	-0.769456	0.000273
0.0140	-0.764447	0.000305	-0.772628	0.000280
0.0160	-0.765899	0.000351	-0.776217	0.000340
0.0180	-0.767640	0.000551	-0.780260	0.000527
0.0190	-0.768647	0.000764	-0.782441	0.000748
0.0200	-0.769726	0.001146	-0.784711	0.001069

Table 2. The energy and the width of the states $2p^2\ ^3P$, M=0 and $2p^2\ ^3P$, |M|=1 of He, as a function of the field strength F of a static electric field.

	$2p^2\ ^3P$, M=0		$2p^2\ ^3P$, |M|=1	
F (a.u.)	E (a.u.)	Γ (a.u.)	E (a.u.)	Γ (a.u.)
0.0000	-0.710218	0.	-0.710218	0.
0.0005	-0.710224	0.0	-0.710212	$\sim 7\times10^{-8}$
0.0010	-0.710241	0.0	-0.710194	0.0000003
0.0020	-0.710308	0.0	-0.710121	0.0000012
0.0030	-0.710421	0.0	-0.710003	0.0000028
0.0040	-0.710579	0.0	-0.709841	0.0000048
0.0050	-0.710784	$\sim 9\times10^{-9}$	-0.709642	0.0000074
0.0060	-0.711035	1.9×10^{-8}	-0.709409	0.0000104
0.0070	-0.711335	3.4×10^{-8}	-0.709151	0.000014
0.0080	-0.711684	5.5×10^{-8}	-0.708876	0.000018
0.0090	-0.712084	1.3×10^{-7}	-0.708597	0.000024
0.0100	-0.712539	5.2×10^{-7}	-0.708333	0.000054
0.0110	-0.713051	1.3×10^{-6}	-0.708071	0.000161
0.0120	-0.713627	4.9×10^{-6}	-0.707828	0.000274
0.0130	-0.714277	0.000023	-0.707647	0.000535
0.0140	-0.715006	0.000105	-0.707449	0.001060
0.0160	-0.716585	0.000391	-0.706736	0.002368
0.0180	-0.718533	0.000778	-0.706022	0.003280
0.0190	-0.719658	0.001191	-0.705722	0.003820
0.0200	-0.720853	0.001845	-0.705313	0.004705

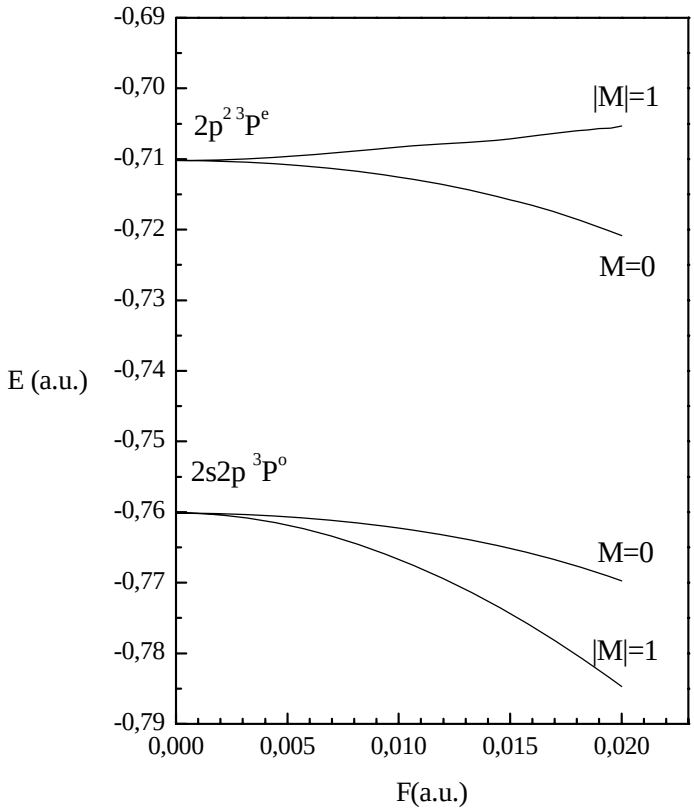

Fig. 1. The energy shift of the states $2s2p\ {}^3P^o$ and $2p^2\ {}^3P$ in a strong static electric field.

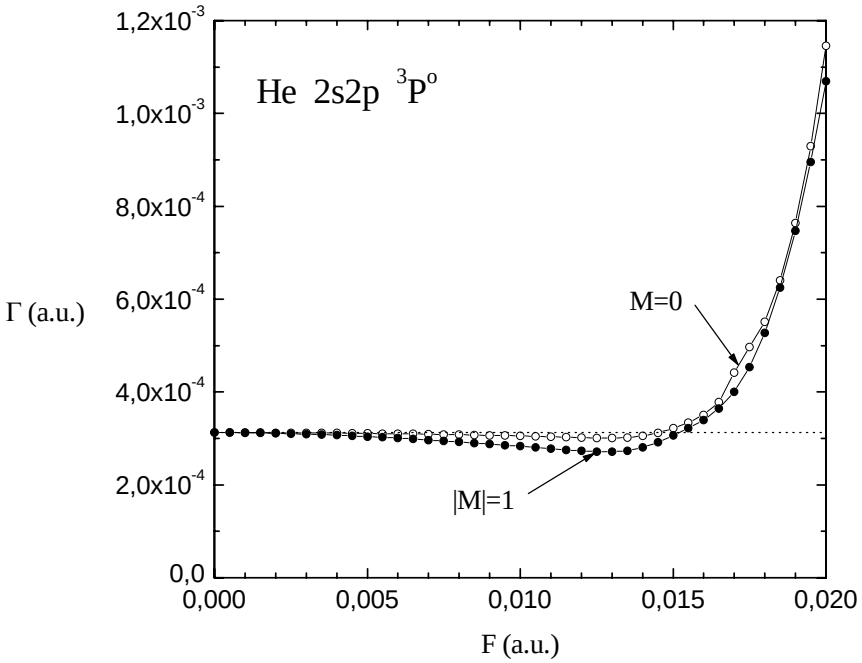

Fig. 2. The width of the states $2s2p\ {}^3P^o$, M=0 and $2s2p\ {}^3P^o$, |M|=1 in a static electric field. The dashed line marks the zero-field width of these states.

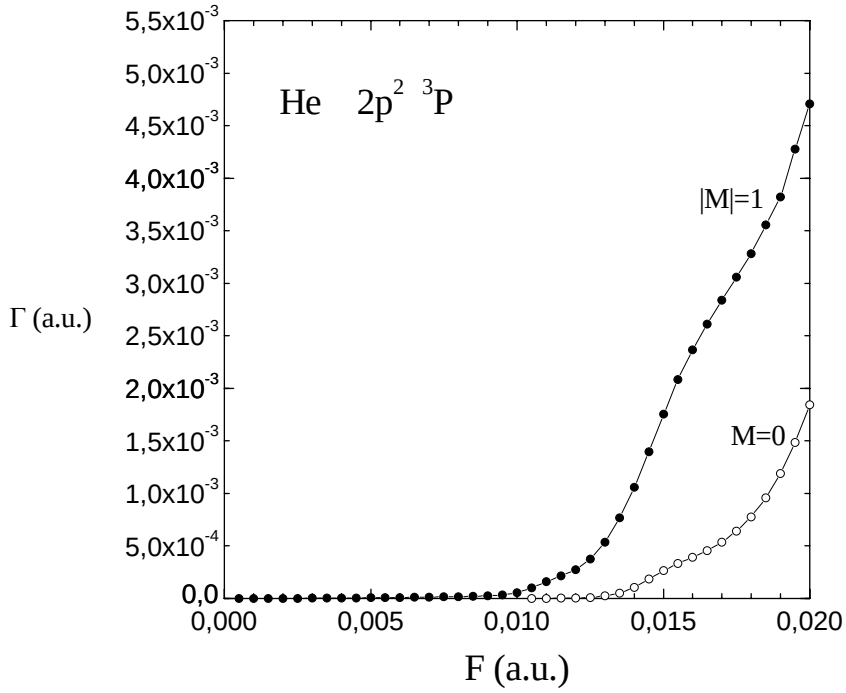

Fig. 3. The field induced width of the states $2p^2\ ^3P$, M=0 and $2p^2\ ^3P$, |M|=1 in a static electric field.

with M = ±1 this decreasing in the width is a bit smaller because of the mixing that exists with the states $2p^2\ ^3P$, M = ±1 and of the transfer of the field-induced width to these states. For the largest value of field for which we performed these calculations the energy width of these states is roughly 30 meV. In figure 1 we present the variation of the energy positions of the states considered here and in figure 2 we present the variation of the corresponding width as a function of the applied external electric field.

The state $2p^2\ ^3P$, M=0 shows negative energy shift, while the states $2p^2\ ^3P$, M = ±1 for the values of the field strength up to F ~0.02 a.u. present positive energy shift. The field-induced width of these states is increased continuously. However, for the states with M = ±1 this change becomes with much higher gradient than for this with M=0. Thus for the largest value of the field strength for which we have done the calculations, the width of these states differs enough. In figure 1 we present the variation of the energy positions of the states considered here and in figure 3 we present the variation of the corresponding width.

It is interesting to note that the polarizability of the state $2p^2\ ^3P$, M=0 calculated here is α_o = 44.9 a.u. and the polarizability of the state $2p^2\ ^3P$, |M| = 1 is α_1 = -48.9 a.u. The calculated polarizabilty of the state $2s2p\ ^3P^o$ M=0 is α_o = 41.2 a.u. and the polarizability of the state $2s2p\ ^3P^o$, |M| = 1 is α_1 =130.8 a.u. These results are in very good agreement with those of ref. [19].

4. Conclusions

We have calculated the field-induced energy shift and the widths of the states $2p^2\ ^3P$ and $2s2p\ ^3P^o$ of He, including all the components of the projection of the total angular momentum on the field axis. The zero-field autoionizing rate of the $2s2p\ ^3P^o$ state plays important role in

the response of the state $2p^2\ ^3P$ with |M|=1 state, since their mixing is more pronounced than the tunnelling. The effects of this mixing could be observed in the photoionization cross section from $1s2s\ ^3S$ or $1s2p\ ^3P^o$ of He or in a scattering experiment with the presence of a DC field. A similar scheme of coupling of these states through a strong laser is possible, since very high intensities are operating nowadays.

Acknowledgements

The author expresses his gratitude for the hospitality of the Physics Department of the University of Cyprus, where a part of this paper was written.

References

[1] A.A. Kiselyov, Int. J. Quant. Chem. 96, 507 (2004).
[2] A.A. Kiselyov, Mold. J. Phys. Sci. 1, 131 (2002).
[3] J. Mahecha, Few-Body Systems 6, 183 (1989).
[4] J.R. Harries, J.P. Sullivan, J.B. Sternberg, S. Obara, T. Suzuki, P. Hammond, J. Bozek, N. Berrah, M. Halka and Y. Azuma, Phys. Rev. Lett. 90, 133002 (2003).
[5] T.K. Fang and K.T. Chung, J. Phys. B: At. Mol. Opt. Phys. 34, 1245 (2001).
[6] N. Ryde, Atoms and Molecules in Electric Fields, Almqvist & Wiksell International, Stockholm, 1976.
[7] M. Halka, Radiation Physics and Chemistry, in press (2006).
[8] M.V. Ammosov, N.B. Delone and V.P. Krainov, Sov. Phys. JETP 64, 1191 (1986).
[9] D. Fisher, Y. Maron, and L.P. Pitaevskii, Phys. Rev. A 58, 2214 (1998).
[10] T. Otobe, K. Yabana, and J.-I. Iwata, Phys. Rev. A 69, 053404 (2004).
[11] C.A. Nicolaides and S.I. Themelis, Phys. Rev. A 45, 349 (1992).
[12] S.I. Themelis and C.A. Nicolaides, J. Phys. B: At. Mol. Opt. Phys. 33, 5561 (2000).
[13] P.A.M. Dirac, The principles of quantum mechanics. Clarendon Press, Oxford, 4th edition (1958).
[14] C.A. Nicolaides and D.R. Beck, Int. J. Quantum Chem. 14, 457 (1978).
[15] Y. Komninos and C.A. Nicolaides, Chem. Phys. Lett. 78, 347 (1981).
[16] W.P. Reinhardt, Int. J. Quantum Chem. Symp. 10, 359 (1976).
[17] I.W. Herbst, Commun. Math. Phys. 64, 279 (1979).
[18] I.W. Herbst and B. Simon, Commun. Math. Phys. 80, 181 (1981).
[19] C.A. Nicolaides and S.I. Themelis, J. Phys. B: At. Mol. Opt. Phys. 26, L387 (1993).