INVESTIGATING THE IONIZATION PROCESS OF NOBLE GAS ATOMS BY A STATIC ELECTRIC FIELD USING SEIGERT STATE METHOD

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ABSTRACT

We investigate the energy shift and ionization rate of noble gas atoms by a static electric field using Siegert state method. The Siegert states of an atom and molecule in a static electric field are the solutions to the stationary Schrödinger equation satisfying specific boundary conditions. Results show that for weak electric field, the energy shift and ionization rate as functions of electric field can be explained by the perturbation and weak-field asymptotic theory, respectively. Nevertheless, these approximation theories fail to explain the behavior of energy shift and ionization rate for strong electric field.

Keywords: ionization, Siegert state, noble gas atoms, static electric field.

TÓM TẮT

Khảo sát quá trình ion hóa của các nguyên tử khí hiếm dưới tác động của điện trường tĩnh sử dụng phương pháp trạng thái Siegert

Chúng tôi khảo sát sự dịch chuyển năng lượng và tốc độ ion hóa của các nguyên tử khí hiếm dưới tác dụng của điện trường tĩnh bằng phương pháp trạng thái Siegert. Trạng thái Siegert của nguyên tử và phân tử trong điện trường tĩnh được xác định là nghiệm của phương trình Schrödinger dừng thỏa mãn những điều kiện biên xác định. Kết quả cho thấy, khi điện trường yếu, sự dịch chuyển năng lượng và tốc độ ion hóa của trạng thái đang xét như là một hàm theo cường độ điện trường có thể được giải thích lần lượt bởi lí thuyết nhiễu loạn và lí thuyết gần đúng trường yếu. Tuy nhiên, các lí thuyết gần đúng này không thể giải thích được biểu hiện của độ dịch chuyển năng lượng và tốc độ ion hóa đối với điện trường mạnh.

Từ khóa: ion hóa, trạng thái Siegert, nguyên tử khí hiếm, điện trường tĩnh.

1. Introduction

The ionization of atoms and molecules by a static electric field is one of the fundamental problems in quantum mechanics. It is the appearance of the intense infrared laser pulses that paves a new wave for the motivated interest in static-field ionization over the past two decades. It is clear that for sufficiently low frequency, the behavior of the ionization in a time-dependent laser field $\mathbf{F}(t)$ is approximately identical to that in a static electric field whose field strength $\mathbf{F}$ equals to the momentary value of $\mathbf{F}(t)$. The ionization of atoms and molecules by a laser field is extremely

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important since it is the first step for variety strong-field induced phenomena of current interest such as the generation of high-order harmonic, high-energy photoelectrons, and nonsequential ionization [2]. For understanding these nonlinear dynamics, the accurate quantitative description of ionization process is obviously required.

The ionization process in a static electric field can be described by the stationary Schrödinger equation whose regular eigensolutions have only outgoing waves in the asymptotic region. The outgoing-wave boundary condition eradicates the hermiticity of the Hamiltonian, hence the solutions exist only for a discrete generally complex value of the energy E as $E = \varepsilon - i\Gamma/2$. The real and the imaginary parts of the SS eigenvalue define the energy ε and the ionization rate Γ of the state. This eigenvalue problem was first initiated by Siegert in 1939 for the derivation of nuclear dispersion formula [8], thus its solutions are called the Siegert states (SSs). By using the Siegert state approach, we can systematically investigate the ionization process of atoms and molecules by a static electric field.

Recently, we have developed a powerful method of adiabatic expansion in parabolic coordinates for calculating one electron SSs in axially symmetric potentials and general potentials without any symmetry. Such potentials can be used to model atoms and molecules in the single-active electron and frozen-nuclei approximations [7]. The method reduces the three-dimensional stationary Schrödinger equation for the SSs to a multichannel eigenvalue problem in one variable, which can be efficiently solved by the slow variable discretization method in combination with the *R*-matrix propagation technique. The detail description of this numerical technique can be found in [1, 4]. We will not mention this numerical technique in this paper since we want to focus on the theory and its application. This method enables us to study the ionization process not only for weak electric field in tunneling regime but also for arbitrary strong field in over-the-barrier regime which cannot be covered by any previous study.

The goal of this paper is to briefly introduce the theory of the Siegert state in a static electric field, then to use this approach to study the ionization process of noble-gas atoms modelled by non-Coulombic core potential. To test the consistency of our results, we compare the energy ε with the perturbation theory, which is a textbook problem [5], and the ionization rate Γ with the recent weak-field asymptotic theory [9] for weak field in the tunneling regime. We also note that there was an attempt to study the ionization of atoms and molecules for strong field at the boundary of tunneling and over-the-barrier regime [11]. However, this work does not based on rigorous mathematic, thus its reliability is still under debate.

The paper is organized as follows. In section 2, we summarize the basis equations of the theory of SSs in an electric field based on the method of adiabatic expansion in parabolic coordinates. In section 3, we present the numerical results for the energy shift and ionization rate, which characterize the ionization process, for the active electron in

the state with $m = 0$ in the outer shells 2*p*, 3*p*, 4*p*, and 5*p* of the noble-gas atoms Ne, Ar, Kr, and Xe, respectively. Section 4 concludes the paper.

2. The theory of Siegert state in a static electric field

The stationary Schrödinger equation describing an electron interacting with an atomic or molecular potential $V(\mathbf{r})$ and a static uniform electric field $\mathbf{F} = F\mathbf{e}_z$, $F \geq 0$, reads (atomic units are used throughout)

$$\left[-\frac{1}{2}\Delta + V(\mathbf{r}) + Fz - E\right]\psi(\mathbf{r}) = 0. \tag{1}$$

The potential $V(\mathbf{r})$ describes the interaction with nuclei and other electrons in the single-active-electron approximation. We assume that

$$V(\mathbf{r})\big|_{r\to\infty} = -\frac{Z}{r}, \tag{2}$$

where *Z* is the total charge of the parent ion. For $F = 0$, equation ((1) has real-energy eigensolutions satisfying $\psi(\mathbf{r})\big|_{r\to\infty} = 0$, which represent bound states of the unperturbed molecule. We solve equation ((1) in parabolic coordinates defined by [5]

$$\begin{aligned} &\xi = r + z, \quad 0 \leq \xi < \infty, \\ &\eta = r - z, \quad 0 \leq \eta < \infty, \\ &\varphi = \arctan\frac{y}{x}, \quad 0 \leq \varphi < 2\pi. \end{aligned} \tag{3}$$

In these coordinates, equation ((1) can be rewritten in the form

$$\left[\frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta} + B(\eta) + \frac{E\eta}{2} + \frac{F\eta^2}{4}\right]\psi(\mathbf{r}) = 0, \tag{4}$$

where the adiabatic Hamiltonian

$$B(\eta) = \frac{\partial}{\partial\xi}\xi\frac{\partial}{\partial\xi} + \frac{\xi+\eta}{4\xi\eta}\frac{\partial^2}{\partial\varphi^2} - rV(\mathbf{r}) + \frac{E\xi}{2} - \frac{F\xi^2}{4} \tag{5}$$

is an operator acting on functions of ξ and φ and depending on η as a parameter. Its eigenvalues and eigenfunctions defined by

$$\begin{aligned} &\left[B(\eta) - \beta_\nu(\eta)\right]\Phi_\nu(\xi,\varphi;\eta) = 0, \\ &\Phi_\nu(\xi = 0,\varphi;\eta) < \infty, \quad \Phi_\nu(\xi\to\infty,\varphi;\eta) = 0, \\ &\Phi_\nu(\xi,\varphi + 2\pi;\eta) = \Phi_\nu(\xi,\varphi;\eta), \end{aligned} \tag{6}$$

also depend on η as a parameter. For any η, the different eigenfunctions of $B(\eta)$ are orthogonal and normalized by

$$\left\langle \Phi_\nu \middle| \Phi_\mu \right\rangle \equiv \int_0^\infty \int_0^{2\pi} \Phi_\nu(\xi,\varphi;\eta)\Phi_\mu(\xi,\varphi;\eta)\,d\xi d\varphi = \delta_{\nu\mu}. \tag{7}$$

The solutions to equations ((6) constitute the adiabatic basis and the functions $\Phi_\nu(\xi,\varphi;\eta)$ are called channel functions. Taking into account equation ((2), the adiabatic Hamiltonian as well as its eigensolutions cease to depend on η in the asymptotic region. Thus the channel functions allow separation of variables and havethe form

$$\Phi_\nu(\xi,\varphi;\eta) = \Phi_{n_\xi m}(\xi,\varphi) = \phi_{n_\xi m}(\xi)\frac{e^{im\varphi}}{\sqrt{2\pi}}. \tag{8}$$

Here $m = 0,\pm1,\pm2,...$ is the azimuthal quantum number and $n_\xi = 0,1,2,...$ enumerates the different solutions to equations ((6) in the asymptotic region. By the analytic continuation in η, we can use the classification $\nu = \left(n_\xi, |m|\right)$ to denote the channel solutions to the adiabatic Hamiltonian ((5).

Having the definition of channel functions $\Phi_\nu(\xi,\varphi;\eta)$, the solution to equation ((4) is sought in the form of an expansion in the adiabatic basis,

$$\psi(\mathbf{r}) = \eta^{-1/2}\sum_\nu f_\nu(\eta)\Phi_\nu(\xi,\varphi;\eta). \tag{9}$$

Substituting this into equation ((4), one obtains a set of ordinary differential equations defining the unknown coefficient functions $f_\nu(\eta)$,

$$\left[\frac{d^2}{d\eta^2} + \frac{1}{2}\left[E - U_\nu(\eta)\right]\right] f_\nu(\eta) + \sum_\mu \left[2P_{\nu\mu}(\eta)\frac{d}{d\eta} + Q_{\nu\mu}(\eta)\right] f_\mu(\eta) = 0, \tag{10}$$

where

$$U_\nu(\eta) = -\frac{1}{2\eta^2} - \frac{2\beta_\nu(\eta)}{\eta} - \frac{F\eta}{2} \tag{11}$$

are the adiabatic potentials and the matrices

$$P_{\nu\mu}(\eta) = \left\langle \Phi_\nu \middle| \frac{\partial\Phi_\mu}{\partial\eta} \right\rangle, \quad Q_{\nu\mu}(\eta) = \left\langle \Phi_\nu \middle| \frac{\partial^2\Phi_\mu}{\partial\eta^2} \right\rangle \tag{12}$$

representing nonadiabatic couplings. Note that in the asymptotic region, these matrices vanish and the equations (10) becomes uncoupled equations. For $F > 0$ and $\arg F = 0$, the outgoing-wave solutions to the uncoupled equations satisfy [1, 9]

$$f_\nu(\eta)\big|_{\eta\to\infty} = \frac{2^{1/2} f_\nu}{(F\eta)^{1/4}} \exp\left[\frac{iF^{1/2}\eta^{3/2}}{3} + \frac{iE\eta^{1/2}}{F^{1/2}}\right]. \tag{13}$$

Here f_ν are the asymptotic coefficients. Their absolute value squared gives the partial width of the SS corresponding to the ionization into the channel ν (see equation (40) in [9]). The SSs are represented by the solutions to equations (10) satisfying regularity boundary condition at $\eta \to 0$ and the outgoing-wave boundary condition ((13) at $\eta \to \infty$. Such solutions exist only for a discrete set of generally complex values of *E*. The real and imaginary parts of the SS eigenvalue *E* define the energy ε and the ionization rate Γ of the state,

$$E = \varepsilon - \frac{i}{2}\Gamma \ . \tag{14}$$

The SS eigenfunction is normalized by

$$\int \psi^2(\mathbf{r})\, d\mathbf{r} = \frac{1}{4}\int_0^\infty \int_0^\infty \int_0^{2\pi} \psi^2(\mathbf{r})(\xi+\eta)\, d\xi\, d\eta\, d\varphi = 1. \tag{15}$$

3. Illustrative results and discussion

We proceed to illustrate the calculation for potentials with non-Coulombic core corresponding to noble-gas atoms which are many-electron systems. However, we restrict our treatment for many-electron atoms within the single-active-electron approximation by utilization of the potential form

$$V(r) = -\frac{Z_{\text{eff}}(r)}{r}, \tag{16}$$

where the effective charge $Z_{\text{eff}}(r)$ monotonically decreases from the bare nuclear charge *N* at $r = 0$, to 1 at $r \to \infty$. Equation ((16) complies with Eq. ((2). We use the simple analytical formula for $Z_{\text{eff}}(r)$ proposed in [3],

$$Z_{\text{eff}}(r) = N - (N-1)\left\{1 - \left[(b/a)\left(e^{ar} - 1\right) + 1\right]^{-1}\right\}. \tag{17}$$

We consider an active electron described by the 2*p*, 3*p*, 4*p* and 5*p* states for Ne, Ar, Kr, and Xe, respectively, with azimuthal quantum number $m = 0$ in all cases. The parameter sets (*a*, *b*) used in practical calculation for Ne(2*p*), Ar(3*p*), Kr(4*p*), and Xe(5*p*) are (1,704; 2,0810), (0,933; 3,600), (1,340; 4,311), and (1,048; 5,197), respectively. Then the field-free energies obtained by using these parameters are more accurate than those presented in [1] and identical to the exact results from more accurate one-electron potentials in [6]. They are -0,793366, -0,579069, -0,515141, and -0,446019, respectively. We also note that in reference [1], the binding energy of Kr was shown to be smaller than that of Xe, which is wrong. Thus to restore the correct order of the binding energies, the parameter used for Kr was modified which is confusing (see Figure (3) in [1]). Such behavior in [1] is due to the improper choice of the parameter sets (*a*, *b*) leading to the poor accuracy of the free-field energies. Hence the present parameters enable us to obtain the correct order of the binding energies of these considered noble-gas atoms.

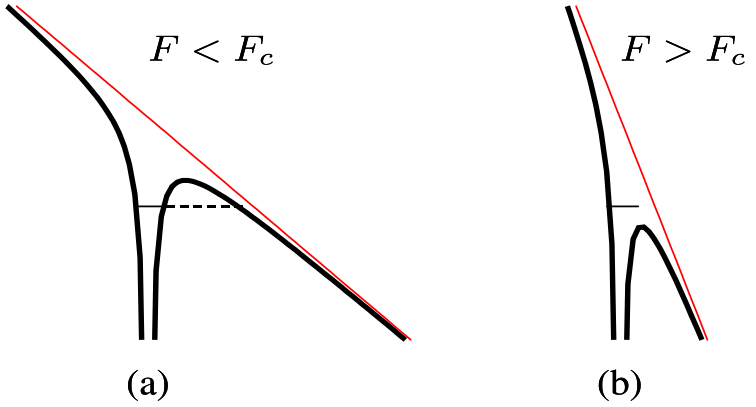

Figure 1. *One-dimensional model for (a) tunneling ionization and (b) over-the-barrier ionization. The thin line corresponds to the contribution from the electric field potential. The thick curve corresponds to the full effective potential energy. The horizontal line represents the free-field bound energy.*

It is instructive to understand the two different mechanisms of ionization process by the electric field before proceeding to the discussion of its behavior. In weak fields, the electron escapes from the atoms or molecules through a finite potential barrier by tunneling mechanism. The barrier becomes thinner and lower as the field increases. For sufficiently strong electric fields, the electron can fly away through a classically accessible window over the potential barrier (see Figure (1)). This is the case of over-the-barrier ionization. In this case the atom or molecule ionizes in about one orbital period. The critical field strength F_c determining the crossover between the tunneling and over-the-barrier regimes can be classically estimated by equating the maximum field-induced effective potential to the ionization potential of the bound electron. The formula estimating F_c is proposed in [9] as

$$F_c = \frac{\aleph^4}{8\left|2Z - \aleph(m+1)\right|}. \tag{18}$$

Here $\aleph = \sqrt{2|E_0|}$ with E_0 is the field-free energy of the considered state. For weak field in the tunneling regime $F \ll F_c$, we compare our numerical results for the real part of SS eigenvalues with the prediction from second-order perturbation theory [5]

$$\varepsilon = E_0 - \alpha \frac{F^2}{2}, \tag{19}$$

and for the imaginary part of SS eigenvalues which defines ionization rate with the leading-order weak-field asymptotic theory (WFAT) [9]

$$\Gamma_{as} = (2 - \delta_{m0})|g_{m0}|^2 W_{m0}(F), \tag{20}$$

where g_{m0} and W_{m0} are the structure factor and the field factor, respectively. The explicit form of g_{m0} and W_{m0} can be referred to equations (59) and (60) of reference [4].

In the practical calculation, several adiabatic channels have to be considered in the expansion ((9) to obtain acceptable convergence up to six significant digits as given previously. Among these channels, note that the lowest channel $\left(n_\xi, m\right) = \left(0,0\right)$ is considered to be dominant within the WFAT, thus the critical fields obtained from equation ((18) for Ne($2p$), Ar($3p$), Kr($4p$), and Xe($5p$) are $F_c = 0,4$, 0,18, 0,13, and 0,09, respectively. In addition, the parameter α and g_{00} used for perturbation and WFAT prediction for these atoms (see equations ((19) and ((20) were derived in [12] as $\left(\alpha; g_{00}\right) = \left(0{,}152; 2{,}1\right)$, (1,323; 2,7), (2,099; 2,3), and (3,079; 2,5), respectively. We consider field in the interval $0 \le F \le 1$, where the upper boundary is well above F_c for all cases.

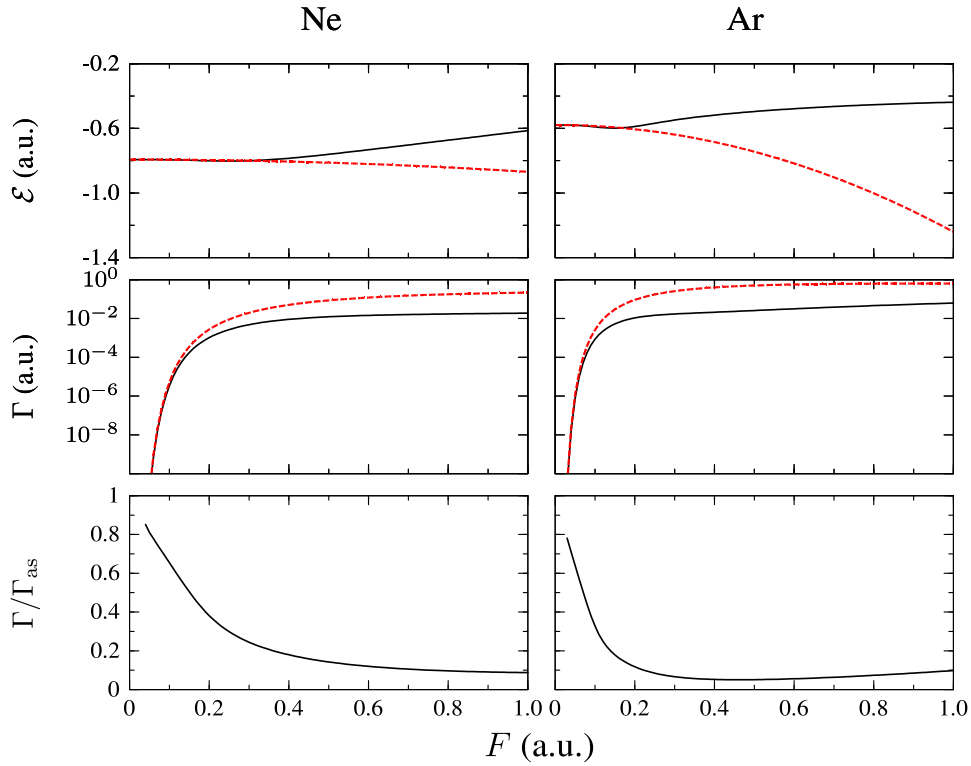

Figure 2. *Energy ε and ionization rate Γ for Ne and Ar as functions of the electric field F. Solid lines for ε and Γ : exact results (from numerical solutions). Dashed lines: results of perturbation theory and asymptotic theory, respectively. Bottom panels: ratio of the exact to the asymptotic results for Γ*

Figures 2 and 3 show the SS eigenvalues for all four noble-gas atoms together with the comparison with results of perturbation theory for the energy ε and leading-order WFAT for the ionization rate Γ as functions of *F*. We also show here the ratio of the exact and WFAT results for Γ as function of *F*. This ratio is useful for gauging the comparison with the WFAT in linear scale. We note that the curve is not continued to smaller F because of a fundamental limitation of the present numerical procedure in calculating very small ionization rates: The procedure yields a complex number *E*, and Γ is obtained from its imaginary part, therefore our calculations with double precision fail if $\Gamma/|E_0| \le 10^{-10}$. In all cases, the energy in the top panels behaves nonmonotonically. First, if goes down quadratically in *F*, in good agreement with the second-order perturbation theory. Then it begins to rise and reaches a maximum, following by rapidly decreasing again. For Xe, it is obvious to see that a maximum appears at $F \approx 0,37$, while the corresponding maximum for Kr is $F \approx 0,97$. The behavior is similar for the two other cases of Ne and Ar. The larger is the binding energy $|E_0|$, the larger *F* at which the maximum happens. Such behavior in the over-the-barrier regime goes beyond the existing theory and only can be observed by our exact numerical calculations. This fact underlines the important role of our present study for accurately quantitative description of the ionization process for strong field in over-the-barrier regime.

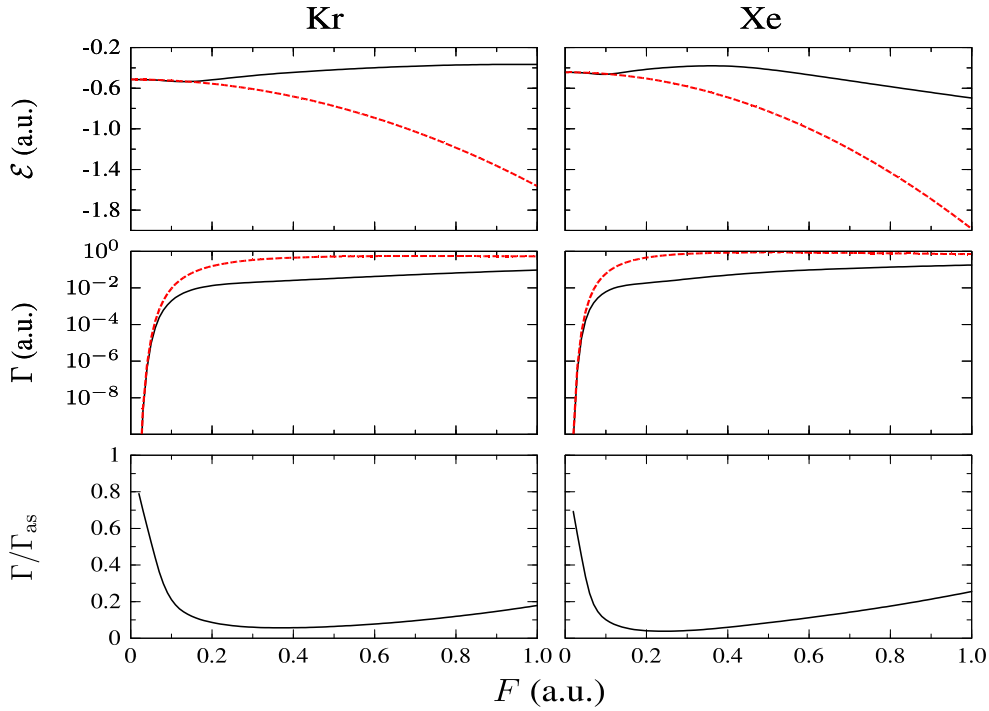

Figure 3. *Similar to Figure 2, but for Kr and Xe*

For sufficiently small F, the ionization rates Γ in the middle panels rapidly decrease with the increase of the binding energy $|E_0|$, so the smallest and largest ionization rates correspond to Ne(2*p*) and Xe(5*p*), respectively, in accordance with equation ((20). The ionization rates first exponentially grow for weak field in the tunneling regime up to the critical field F_c, then still increase but less rapidly, almost linearly, for strong field in the over-the-barrier regime. This fact clearly reflects two different ionization mechanisms as stated above.

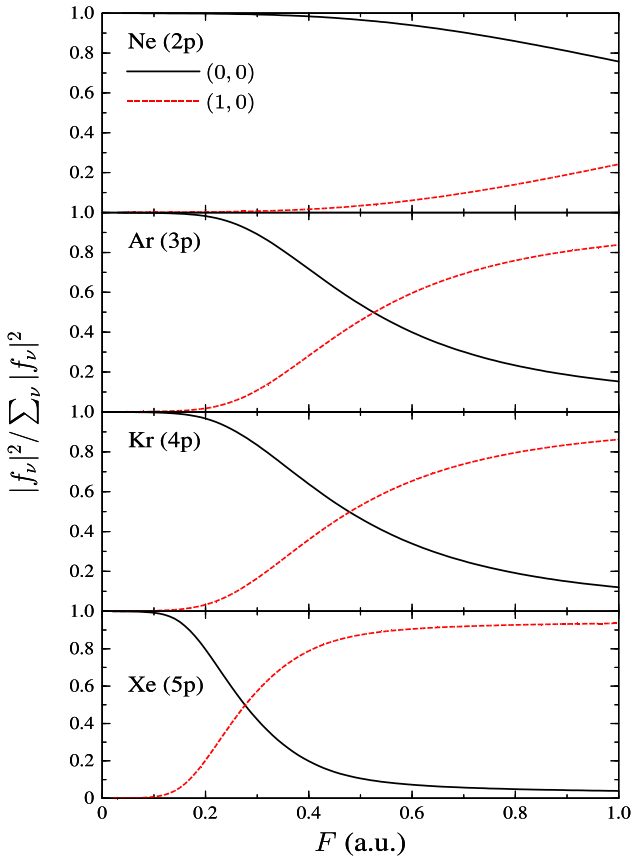

Figure 4. *The asymptotic coefficients f_ν in equation (((13), squared and normalized,as functions of F for four noble-gas atoms*

For all noble-gas atoms, the ratios of exact and asymptotic ionization rate Γ / Γ_{as} approach to unity in the limit $F \to 0$ as expected. A peculiar behavior can be seen here is that the ratio Γ / Γ_{as} first decrease, but begin to rise again, having a minimum at some intermediate *F*. For instance, for Xe(5*p*), the minimum occurs at $F \approx 0,2$. The same happens or the other atoms at larger values of *F* with the order corresponds to the ascending order of the binding energy $|E_0|$. This fact indicates that the leading-order

WFAT seems to work well not only in the tunneling regime, $F \ll F_c$, but also in the over-the-barrier regime, $F > F_c$, which is totally wrong. Such peculiarity stems from the drawback of the WFAT that takes into account the distribution from only one dominant ionization channel, namely the channel (0, 0) in this present case. This explanation is elucidated in the Figure 4 manifesting the coefficients f_v, squared and properly normalized, that determine the relative role of the different channels in equation ((9). For $F \to 0$ only f_{00} survives. For larger *F*, f_{01} emerges to be comparable to f_{00} and finally be dominant. The decrease of the contribution from the channel (0, 0) results in the depression of Γ_{as}, hence the enhancement of the ratio Γ / Γ_{as} is to be observed. Note that for all four noble-gas atoms in the interval of *F* under consideration, the ionization occurs in the lowest two channels. We also note that even for the first-order correction WFAT introduced in [12], such evolution of Γ / Γ_{as} as a function of F is not available. Since this correction was done only for a single dominant channel (0, 0) along with bypassing the vital distribution from channel (1, 0), hence it works well up to the boundary F_c of the over-the-barrier regime. Meanwhile, the maximum field amplitude in currently available laser pulses far exceeds F_c. Thus the role of exact calculation is proved to be indispensable for the study of ionization process in the over-the-barrier regime $F > F_c$.

4. Conclusion

In this paper, we introduce the theory of Siegert state in a static electric field. The major property of the Siegert state is that its eigenvalue provides us not only the energy ε but also the ionization rate Γ of the considered state from its real and imaginary parts, respectively. These quantities are important since they characterize the interaction of atoms and molecules with a static electric field. We use this approach for the investigation of the ionization process of the four noble-gas atoms. We present the illustrative results for the energy and ionization rate as functions of electric field *F* for a wide range of *F* from tunneling to over-the-barrier regimes. For checking the validity of our method, we compare the numerical results to the weak-field approximation theories such as the second-order perturbation theory and leading-order WFAT for the energy and the ionization rate of the state, respectively. The results show that the exact calculations well consists with these weak-field approximations for weak field in the tunneling regime as expected. However, these approximations totally fail to explain the behavior of the exact results for strong field in the over-the-barrier regime. That underlines the indispensable role of our numerical approach.

It is also instructive to emphasize the connection between the atomic SSs in a static electric field and the oscillating laser pulse which is used widely in experiment. All the characteristics of the atomic SSs considered in this paper are the heart of so-called adiabatic theory first initiated in reference [11] used for the study of the ionization of atoms by intense low-frequency laser pulses. This is considered to be the practical virtue of atomic SSs in a static electric field.

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