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Coulomb and Coulomb-Stark Green-function approach to adiabatic Rydberg energy levels of alkali-metal—helium systems

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The adiabatic Σ electronic terms of highly excited states of the He—alkali-metal atom systems are determined as the roots of a transcendental equation whose only required inputs are the alkali-metal quantum defects, the e^--He s-wave phase shifts and, of course, the internuclear distance R. The results obtained for relatively low excited states are in reasonable agreement with more elaborate calculations. It is found that the notion of adiabatic quantum defects requires $R(\text{a.u.}) \lesssim 2n$, n being the principal quantum number. The method is generalized to the case where a small external electric field $\mathscr{E}$ is present. Then the energy levels strongly depend on the angle between $\mathscr{E}$ and the internuclear axis. Numerical applications to He-H are presented.

I. INTRODUCTION

Adiabatic energy levels for systems consisting of a Rydberg atom and a ground-state rare-gas atom at an internuclear distance R have been the subject of numerous theoretical works (see, e.g., Refs. 1—12 and reference therein). The subject is of interest for the investigation of pressure effects on the spectral lines of highly excited atoms, and for analyzing very-low-energy collisions processes. It also is an interesting theoretical challenge as *ab initio* variational calculations require a large basis set of wave functions for highly excited states and therefore seem to be inadequate. The way to bypass these difficulties traces back to Fermi.[1] The presence of the rare-gas atom inside the Rydberg atom is interpreted as a modification of the boundary conditions for the electronic wave function. This idea, which is the same as the one of quantum-defect theory (see, e.g., Refs. 13 and 14) then allows one to express the adiabatic energy levels in terms of scattering data for low-energy collisions between a free electron and the rare gas. In its most elementary form, the shifts of energy levels are determined using the popular Fermi pseudopotential[15] $2\pi L\delta^{(3)}(\mathbf{R}-\mathbf{r})$ within first-order perturbation theory. L is the e^-—rare-gas scattering length, and $\mathbf{r}$ refers to the e^- position vector. It should be noted, however, that the use of the Fermi pseudopotential within a diagonalization procedure is not very convenient for highly excited states as the presence of numerous nearly degenerate states may require a large truncated basis. A more elaborate formulation, which is not a perturbative one, is obtained when using the explicit expression for the Coulomb Green function, as done for instance in Refs. 7—12 and in the present paper.

Section II of this paper derives the basic equations [Eqs. (24)] for determining adiabatic energy levels Σ in a simple, self-contained way. It does not require any acquaintance with quantum-defect theory, or multiple-scattering theory. To first order in the expansion of the cotangent of the s-wave phase shift for the e^--He scattering, the result is essentially the one obtained in 1972 by Dalidchik and Ivanov[9] in a paper apparently not well known, as it appears to be ignored in numerous subsequent publications on the topic. It is also found in Sec. II that the notion of an adiabatic quantum defect requires $R \lesssim 2\nu$, where $-\mu/(2\nu^2)$ corresponds to the adiabatic energy. μ represents the reduced mass of the electron and the alkali-metal core in a.u. From this point on, μ will be replaced by unity in the formulas, for the sake of simplicity.

To our knowledge, no application of the method of Dalidchick and Ivanov[9] has been made to alkali-metal-atom—rare-gas systems. Recently,[16] there have been some results concerning relatively low excited states of the Na-He systems on the basis of the model-potential approach. It is therefore of interest to compare the results presently obtained with these more elaborate calculations. This is the purpose of Sec. III. As explained in Sec. II, the present approach requires the e^-—rare-gas interaction be short range. The helium atom, having a small polarizability, is therefore a good candidate. Comparisons for the Na-Ne system are, however, also reported in Sec. III, in order to test the influence of polarization effects. Finally, variation of the adiabatic quantum defects with the internuclear distances are also presented in Sec. III.

Section IV extends the result of Sec. II to the cases where a small external electric field $\mathscr{E}$ is present. The adiabatic energy levels then depend on the angle θ between $\mathscr{E}$ and the internuclear axis R. Numerical applications for the system H-He are presented. Section V discusses and concludes the work.

It is important to note here that throughout this paper, the term adiabatic energy levels means the adiabatic electronic energies, and does not include the interaction between the positive alkali-metal core and the rare gas. This last term, which is an additive one, has never been taken into account. The results are then directly related to molecular ionization energies.

II. BASIC FORMULATION

A. Basic Hamiltonian and its significance

In order to take into account the modifications of the boundary conditions for the electronic wave functions, required by the presence of He and the alkali-metal core structure, we believe that the most convenient way is to introduce separable short-range interactions in the electronic Hamiltonian:

$$H=p^2/2-1/r+\sum_l V_l+V_\rho \tag{1}$$

with

$$V_l\equiv a_l \sum_{m=-l}^{l} r_l^{3/2}\,|\,r_l,l,m\,\rangle\langle\,r_l,l,m\,|\,r_l^{3/2}\ , \tag{2}$$

$$V_\rho\equiv\alpha\,|\,\xi\rangle\langle\xi\,|\ , \tag{3a}$$

$$|\,\xi\rangle\equiv\exp(-i\mathbf{R}\cdot\mathbf{p})\rho^{3/2}\,|\,r=\rho,l=0,m=0\rangle\ . \tag{3b}$$

The kets $|\,r_l,l,m\,\rangle$ are defined by

$$\langle\,\mathbf{r}\,|\,r_l,l,m\,\rangle=Y_l^m(\hat{\mathbf{r}})\delta(r-r_l)/r^2\ ,$$

where Y denotes spherical harmonics with respect to an arbitrary axis z. The sum over l in Eq. (1) runs only over l values associated with nonzero alkali-metal quantum defects d_l ($l\leq3$). The terms V_l correspond to the departure from a pure Coulomb field due to the alkali-metal core. The term V_ρ is a projector onto the s wave relative to He, and is sufficient to describe the e^--He interaction at low energy where the s-wave contribution is dominant. The factors $r_l^{3/2}$ and $\rho^{3/2}$ in Eqs. (2) and (3b) are just a matter of convenience in order that a_l and α have the dimension of an energy.

Among the Σ eigenvalues of H [Eq. (1)], those, to be denoted $-1/(2\nu^2)$, which are different from the hydrogenic eigenvalues $-1/(2n^2)$, are easily shown to be solutions of

$$\det A=0 \tag{4a}$$

with A an Hermitian matrix of dimension equal to the number of nonzero quantum defects plus one, and defined by

$$A_{11}=\langle\xi\,|\,G(\nu)\,|\,\xi\rangle-1/\alpha\ , \tag{4b}$$

$$A_{1,l+2}=r_l^{3/2}\langle\xi\,|\,G(\nu)\,|\,r_l,l,0\rangle=A_{l+2,1}^{*}\ , \tag{4c}$$

$$A_{l+2,l+2}=r_l^3\mathcal{G}_l(\nu,r_l,r_l)-1/a_l\ , \tag{4d}$$

all other matrix elements being equal to zero. $G(\nu)$ is the Coulomb-Green operator

$$G(\nu)\equiv[-1/(2\nu^2)-p^2/2+1/r]^{-1} \tag{5a}$$

and the m independent function $\mathcal{G}_l$ is defined by

$$\mathcal{G}_l(\nu,r,r')\equiv\langle\,r,l,m\ |\,G(\nu)\,|\,r',l,m\,\rangle\ . \tag{5b}$$

At this stage, some remarks are necessary. First, the introduction from the outset of an interaction V_ρ of range $\rho\neq0$ is an advantage since a subsequent expansion in a power series of ρ will be responsible for taking into account the classical local momentum of the Rydberg electron. Second, all the parameters a_l,r_l,α,ρ appear only, at the end of the calculation, through their associated physical data, i.e., quantum defects and scattering phase shift (see Sec. II B). The Hamiltonian H of Eq. (1) certainly does not represent any "realistic" interaction. It is only a very convenient tool in the search for the expected general relation between adiabatic energy levels and physical atomic data. Thus a general relation is expected to be approximately valid for any short-range interaction.[1,9] The most critical point is then to incorporate the long-range polarization interactions into the effective short-range interactions, as is done when using the experimental atomic data for alkali-metal quantum defects and s-wave phase shifts for e^-—rare-gas scattering. The discussion of this point is postponed to the end of Sec. III.

B. Solution in terms of physical data

The scattering of a free electron of kinetic energy $p^2/2$ by the separable potential V_ρ is exactly soluble. All the information is contained in the s-wave phase shift $\delta(p)$ determined by:[17]

$$\cot\delta(p)=[1/\alpha-\mathrm{Re}\langle\xi\,|\,G_0(p^2/2+i\epsilon)\,|\,\xi\rangle]/[\mathrm{Im}\langle\xi\,|\,G_0(p^2/2+i\epsilon)\,|\,\xi\rangle] \tag{6}$$

with the free Green operator,

$$G_0(z)=(z-p^2/2)^{-1}\ . \tag{7}$$

Now the term A_{11} of Eq. (4a) can be written as

$$A_{11}=-1/\alpha+\int d^3r_1d^3r_2\langle\xi\,|\,\mathbf{r}_1\rangle \times\langle\mathbf{r}_1\,|\,G(\nu)\,|\,\mathbf{r}_2\rangle\langle\mathbf{r}_2\,|\,\xi\rangle \tag{8}$$

with[18]

$$\langle\mathbf{r}_1\,|\,G(\nu)\,|\,\mathbf{r}_2\rangle =[\Gamma(1-\nu)/(2\pi y)]\partial/\partial(y/\nu) \times[W_{\nu,1/2}((2x+y)/\nu)\mathcal{M}_{\nu,1/2}((2x-y)/\nu)]\ , \tag{9}$$

where $y=|\,\mathbf{r}_1-\mathbf{r}_2\,|$, $2x=r_1+r_2$. W and $\mathcal{M}$ are the Whittaker functions as defined in Ref. 19, satisfying the second-order differential equation

$$\ddot{f}(2x/\nu)=-(\nu p_x/2)^2f(2x/\nu) \tag{10}$$

where $y=|\,\mathbf{r}_1-\mathbf{r}_2\,|$, $2x=r_1+r_2$. W and $\mathcal{M}$ are the Whittaker functions as defined in Ref. 19, satisfying the second-order differential equation

$$p_x^2=2/x-1/\nu^2\ . \tag{11}$$

Developing the product of Whittaker functions in Eq. (9) in a Taylor series in the vicinity of $2x/\nu$, using Eq. (10) and neglecting all derivatives of p_x, one obtains the quasiclassical approximation[12]

$$\langle \mathbf{r}_1 | G(\nu) | \mathbf{r}_2 \rangle \simeq -(2\pi y)^{-1}[\cos(yp_x)+h(\nu,x)\sin(yp_x)/p_x] \tag{12}$$

with

$$h(\nu,x)=[2\Gamma(1-\nu)/\nu][\dot{W}_{\nu,1/2}\dot{\mathscr{M}}_{\nu,1/2} + (\nu p_x/2)^2 W_{\nu,1/2}\mathscr{M}_{\nu,1/2}] , \tag{13}$$

where the argument of the Whittaker functions is $2x/\nu$. This approximation requires $y/\nu \ll 1$. In Eq. (8), one has $R-\rho \le r_i \le R+\rho$, $i=1,2$. For R large enough and ρ small enough, $r_1+r_2 \simeq 2R$ in Eq. (12). Recalling that

$$\langle \mathbf{r}_1 | G_0(p_R^2/2+i\epsilon) | \mathbf{r}_2 \rangle = -(2\pi y)^{-1}\exp(ip_R y) \tag{14}$$

one then obtains a quasiclassical expression for A_{11},

$$A_{11} \approx -1/\alpha + \mathrm{Re}\langle \xi | G_0(p_R^2/2+i\epsilon) | \xi \rangle + h(\nu,R)\mathrm{Im}\langle \xi | G_0(p_R^2/2+i\epsilon) | \xi \rangle / p_R . \tag{15}$$

Now, recalling that

$$\langle \xi | G_0(p_R^2/2+i\epsilon) | \xi \rangle = -2\rho^2 \exp(i\rho p_R)[\sin(\rho p_R)]/(\rho p_R) \simeq -2\rho^2 \exp(i\rho p_R) \tag{16}$$

as $\rho p_R < 1$, A_{11} finally can be expressed as a function of the physical phase shift $\delta(p)$,

$$A_{11} \simeq 2\rho^3[p_R \cot\delta(p_R) - h(\nu,R)] . \tag{17}$$

In the purely hydrogenic case, the adiabatic energy levels are obtained by solving $A_{11}=0$. Taking the first-order term in the expansion of $p\cot\delta(p)$, i.e., $-1/L$, one recovers the result of Komarov[7] and Presnyakov.[8] The idea of a classical coupling between the electron position and its momentum [Eq. (11)] has been used by several authors (see, e.g., Refs. 3 and 10).

For nonhydrogenic cases, the other elements of the matrix A must be evaluated. For $A_{1,l+2}$, one obtains by including one closure relation in Eq. (4c),

$$A_{1,l+2} = (r_l^{3/2}\sqrt{\pi\rho}/R) \int_{R-\rho}^{R+\rho} dr\, r Y_l^0(\theta) \mathscr{G}_l(\nu,r,r_l) \tag{18}$$

with $\cos\theta = (R^2+r^2-\rho^2)/(2Rr)$. If R is large compared to ρ, $\theta \simeq 0$ and $\mathscr{G}_l(\nu,r,r_l) \simeq \mathscr{G}_l(\nu,R,r_l)$ so that

$$A_{1,l+2} \simeq \rho^{3/2} r_l^{3/2} \sqrt{(2l+1)}\, \mathscr{G}_l(\nu,R,r_l) \tag{19}$$

with[18]

$$\mathscr{G}_l(\nu,R,r_l) = -[\nu/(r_l R)]\Gamma(1+l-\nu) \times W_{\nu,l+1/2}(2R/\nu)\mathscr{M}_{\nu,l+1/2}(2r_l/\nu) . \tag{20}$$

For $r \lesssim 2\nu$, $\mathscr{M}$ can be expressed in terms of Bessel functions [Appendix, Eq. (A1)]. Thus,

$$A_{1,l+2} \simeq -\rho^{3/2} r_l \sqrt{2(2l+1)} J_{2l+1}(\sqrt{8r_l})\Gamma(1+l-\nu) \times \nu^{-l} R^{-1} W_{\nu,1/2}(2R/\nu) . \tag{21}$$

There remains finally the task of evaluating $A_{l+2,l+2}$. The exact solution of the atomic Hamiltonian $p^2/2 - 1/r + \sum_l V_l$ provides a relation between a_l and the physical quantum defects d_l,

$$\mathscr{G}_l(n-d_l, r_l, r_l) = 1/(a_l r_l^3) . \tag{22}$$

For both $r \lesssim 2\nu$ and $l/\nu \ll 1$, W can be expressed in terms of the Bessel functions [Eq. (A3)], so that

$$A_{l+2,l+2} \simeq 2\pi r_l^2 J_{2l+1}^2(\sqrt{8r_l})[\cot(\pi\nu)+\cot(\pi d_l)] . \tag{23}$$

From Eqs. (17), (21), and (23) it is seen that the condition $\det A = 0$ reduces to

$$\det P = 0 \tag{24a}$$

with the matrix P involving only physical atomic data,

$$P_{11} = p_R \cot[\delta(p_R)] - h(\nu,R) , \tag{24b}$$

$$P_{1,l+2} = -\sqrt{(2l+1)/(2\pi)}\,\Gamma(1+l-\nu) \times \nu^{-l} R^{-1} W_{\nu,l+1/2}(2R/\nu) = P_{l+2,1} , \tag{24c}$$

$$P_{l+2,l+2} = \cot(\pi\nu) + \cot(\pi d_l) , \tag{24d}$$

all other matrix elements being equal to zero. The equation (24a) $\det P = 0$ provides the adiabatic energies $-1/(2\nu^2)$ in terms of the alkali-metal quantum defects d_l and the s-wave phase shift of e^-—rare-gas scattering. In the case of one quantum defect and within the approximation $p\cot[\delta(p)] \simeq -1/L$ one recovers the result of Dalidchik and Ivanov.[9]

In the last part of this section it is seen that for $R \lesssim 2\nu$ the adiabatic energies take the limiting form $-1/\{2[n-d(R)]^2\}$ with n an integer and $d(R)$ an adiabatic quantum defect. For $R \lesssim 2\nu$ the Whittaker functions in Eqs. (24b) and (24c) can be expressed in terms of Bessel functions [Eqs. (A1) and (A3)]. Using Eq. (11) and the further approximations[20]

$$J_0(\sqrt{8R})Y_0(\sqrt{8R}) + J_1(\sqrt{8R})Y_1(\sqrt{8R}) \simeq 0 , \tag{25a}$$

$$J_0^2(\sqrt{8R}) + J_1^2(\sqrt{8R}) \simeq (\pi\sqrt{2R})^{-1} , \tag{25b}$$

valid if $R \gtrsim 5$, one obtains

$$P_{11} \simeq \sqrt{2/R}\,\{\cot[\delta(\sqrt{2/R})] + \cot(\pi\nu)\} , \tag{26a}$$

$$P_{1,l+2} \simeq 2\sqrt{2\pi(2l+1)} \times [Y_{2l+1}(\sqrt{8R}) + \cot(\pi\nu)J_{2l+1}(\sqrt{8R})]/\sqrt{8R} . \tag{26b}$$

The P matrix [Eqs. (26a), (26b), and (24d)] then becomes a periodic function of ν, with period unity.

C. A qualitative feature of the spectra

Before coming to quantitative results (Sec. III), an important qualitative property of the adiabatic energy spectra must be emphasized. If a discrete eigenvalue ε_i of a Hamiltonian $\mathscr{H}$ has a degeneracy degree n_i, then the addition of a separable potential $\alpha|\xi\rangle\langle\xi|$ to $\mathscr{H}$ leaves $n_i - 1$ states unaffected and reduces the degeneracy at most by one degree. This can be seen as follows. An eigenvalue z of $\mathscr{H}' = \mathscr{H} + \alpha|\xi\rangle\langle\xi|$ different from the eigenvalues ε_i of $\mathscr{H}$ must satisfy the equation

$$\langle \xi | (z-\mathscr{H})^{-1} | \xi \rangle - 1/\alpha = 0 \ . \tag{27a}$$

z is nondegenerate as its corresponding eigenvectors must be proportional to $(z-\mathscr{H})^{-1} | \xi \rangle$. Using the spectral representation of $(z-\mathscr{H})^{-1}$, Eq. (27a) takes the form

$$-1/\alpha + \sum\!\!\!\!\!\!\int (z-\varepsilon_i)^{-1} f_i = 0 \tag{27b}$$

with the positive numerators f_i defined by

$$f_i = \sum_{\{j\}} |\langle \xi | \varphi_{i,\{j\}} \rangle |^2 \ ,$$

where $\{j\}$ denotes the set of quantum numbers defining an eigenstate $|\varphi_{i,\{j\}}\rangle$ of $\mathscr{H}$, with energy ε_i. The left-hand side of Eq. (27b) is clearly a decreasing function of z for z between two successive poles $\varepsilon_i, \varepsilon_{i+1}$. Thus, Eq. (27a) has only one root between ε_i and ε_{i+1} (it may have no root in the cases where f_i or f_{i+1} is zero).

The question now arises why this property is also relevant to the physical problem of interest, i.e., alkali-metal Rydberg states perturbed by He. This can be understood as follows. For an atomic excited state, as the distance from the nucleus increases, the electronic wave function oscillates more and more slowly in the classical domain. Thus, except at small internuclear distances from the nucleus, the e^--He interaction looks more and more pointlike with respect to the local period of oscillation of the wave function. If a pointlike interaction is diagonalized within a set of degenerate states, as done when using the Fermi pseudopotential, it is possible to perform a change of basis such that all, except one new wave function, are zero at the point of interaction (see, e.g., Ref. 6). Thus, except in the cases where all the wave functions are zero at the point considered, the degeneracy is reduced by one degree.

This qualitative property seems less justified at small internuclear distances where the wave functions oscillate more rapidly. It should be noted, however, that for a given value of l, the hydrogenic wave functions are essentially zero in the nonclassical domain

$$r < n^2\{1-[1-l(l+1)/n^2]^{1/2}\} \simeq l(l+1)/2 \ .$$

Thus, among the n^2 degenerate hydrogenic wave functions only those corresponding to small values of l are to be taken into account at small internuclear distances. Moreover, for alkali-metal atoms the levels with small values of l are no longer degenerate with the hydrogenic levels, so that the problem is avoided. For hydrogen however, the rare-gas atom could reduce the degeneracy by more than one degree at small internuclear distances, contrary to the prediction of the present approach.

III. NUMERICAL APPLICATIONS

The best way to test the present results [Eqs. (24)] is to compare them with the results of more elaborate calculations taking explicitly into account long-range forces due to polarization effects. The most excited Σ levels we have found for which such calculations have been published[16] are the $6p$,$5x$ levels of Na-He. The letter x is for a level which correlates to the hydrogenic level $-\mu/(2n^2)$.

It is seen in Fig. 1 that the agreement between the results given by Eqs. (24) and the results of Valiron *et al.*[16] is surprisingly good for such low principal quantum numbers, except at small internuclear distances for the $5x$ level. For $p_R \cot[\delta(p_R)]$ we have used spline interpolation from the experimental results of Williams[21] together with the value $-1/L$, $L=1.19$, at zero energy. It should be noted that for $R>2v^2$, p_R becomes imaginary. In those cases, $\delta(p_R)$ could still be extracted from experimental data within the framework of effective-range theory. In the present paper we use $-1/L$ for $p_R \cot[\delta(p_R)]$ if the case $R>2v^2$ occurs. In such cases the asymptotic levels are generally already reached. In Fig. 1 we also report the results obtained if the term $p_R \cot[\delta(p_R)]$ is replaced by $-1/L$ for all R values in Eq. (24b). It is seen that the agreement with the results of Valiron *et al.*[16] is then no longer as good, especially for the $6p$ level at small internuclear distances.

Figure 2 reports the same comparisons for the Na-Ne case. $p_R \cot[\delta(p_R)]$ was again calculated from the experimental results of Williams[21] together with the value $-1/L$, $L=0.24$, at zero energy. As the neon has a greater polarizability than helium, the comparison is expected to be less favorable. However, it still remains good. The importance of taking into account the classical local momentum of the Rydberg electron is manifest in Fig. 2, especially for the $5x$ level. The scattering cross section for e^--Ne collision varies indeed much more with the energy than for e^--He collision. This point was also noted in Ref. 16 within the framework of the Fermi pseudopotential.

In order to see the limits of the present method, we have considered still more lower levels, and for the alkali-metal atom exhibiting the greatest polarizability, i.e., cesi-

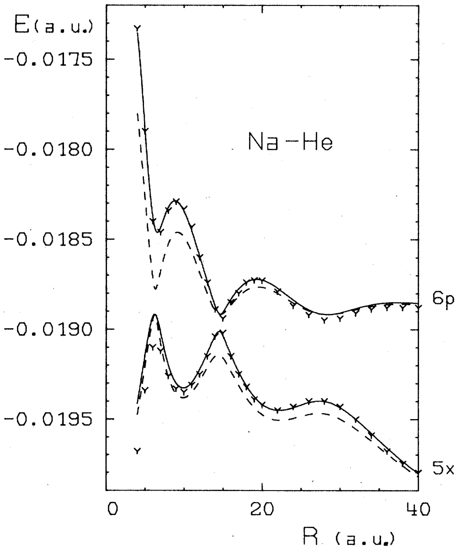

FIG. 1. Adiabatic ionization energies for Σ_{5x} and Σ_{6p} levels of Na-He. Solid curves: present results computed from Eqs. (24). Y data of Valiron *et al.*, reported from Fig. 9 of Ref. 16. Dashed curves: results computed from Eqs. (24) when $p_R \cot[\delta(p_R)]$ is approximated by $-1/L$.

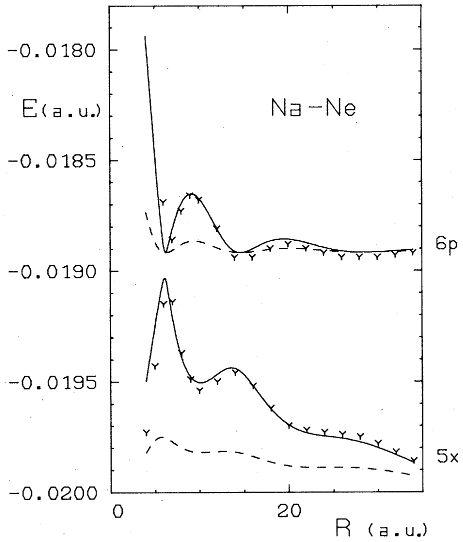

FIG. 2. Adiabatic ionization energies for Σ_{5x} and Σ_{6p} levels of Na-Ne. As in Fig. 1. Y data reported from Fig. 10, Ref. 16.

um. Fine structure is not taken into account. Comparison with the results of Pascale[22] obtained by using a pseudopotential method are reported in Fig. 3 for the $8s$, $6d$, $7p$ levels of Cs-He. It is seen that the agreement is only qualitative for the $6d$ level. A possible explanation of this fact is that the energy of the considered levels, about -0.04 a.u., to be compared to -0.02 a.u. in the preceding cases of Na-He, Na-Ne (see Figs. 1 and 2), is too low; for such energies, the conditions $l/\nu \ll 1$ are not well satisfied, and the polarization of Cs may be too large for the present method to be valid.

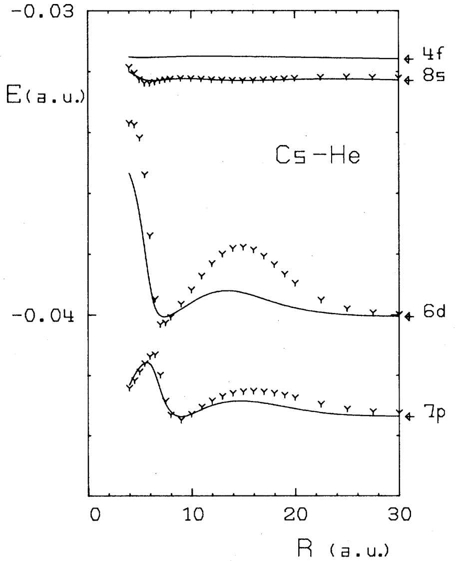

FIG. 3. Adiabatic ionization energies for some excited Σ levels of Cs-He. Solid curves: present results computed from Eqs. (24). Y results of Pascale (Ref. 22), when the core-core interaction has been removed.

In Sec. II A the question was whether or not incorporating polarization effects into effective short-range interactions, as done when solving Eqs. (24) with experimental atomic data for d_l, δ, is a reasonable approximation. The comparisons carried out above provide a positive answer, at least for light atoms. For heavier rare-gas atoms (Ar, Kr, Xe) having a larger polarizability, the question still remains open. For these heavier rare gases, a more refined treatment of polarizability effects may be necessary. A method for isolating polarization effects in a perturbative treatment has been proposed by Ivanov.[23]

Finally, graphs in Fig. 4 report the fractional part $D(R)$ of the quantum defects $d(R)$ for H-He and the alkali-metal—He systems, computed according to Eqs. (24a), (26a), (26b), and (24d). It is recalled that the notion of adiabatic quantum defects requires $R \lesssim 2\nu$. For the quantum defects d_l of the alkali atoms, we use the values reported in Table III of Ref. 24. Fine structure has not been taken into account. It is seen that the Σ_x quantum defects do not reach the hydrogenic asymptotic value [$D=1$ in Figs. 4(a)—4(f)] for $R=100$ a.u. For this value of R it can be seen that the value of the Σ_x quantum defects are approximately the same for hydrogen and all alkali metals. The asymptotic values for the $\Sigma_{s,p,d,f}$ quantum defects are, to the contrary, reached much more rapidly.

IV. INFLUENCE OF A SMALL ELECTRIC FIELD $\mathscr{E}$

By small field, we mean within the domain of the linear hydrogenic Stark effect. The rare-gas atom has polar coordinates $R,\theta,\varphi=0$, relative to a frame x,y,z centered on the alkali-metal nucleus and whose axis z is parallel to $\mathscr{E}$. The Hamiltonian therefore becomes

$$H=p^2/2-1/r+\sum_l V_l+e^{-i\theta L_y}V_\rho e^{i\theta L_y}+\mathscr{E}z \tag{28}$$

with V_l and V_ρ defined by Eqs. (2) and (3a) where now

$$|\xi\rangle=\exp(-iR\hat{\mathbf{z}}\cdot\mathbf{p})\rho^{3/2}\,|\rho,0,0\rangle \tag{29}$$

and the kets $|\,r,l,m\,\rangle$ are defined relative to z,

$$L_z\,|\,r,l,m\,\rangle=m\,|\,r,l,m\,\rangle\ . \tag{30}$$

The adiabatic energy levels are now functions of R and θ. All the procedures of Sec. II can be repeated with $G_S(\nu)$, the Coulomb-Stark Green operator given by

$$G_s(\nu)\equiv[-1/(2\nu^2)-p^2/2+1/r-\mathscr{E}z]^{-1} \tag{31}$$

in place of $G(\nu)$ [Eq. (5a)]. Two main differences, however, occur. First, $G_s(\nu)$ commutes only with L_z and no longer with L^2. Second, the $\langle\mathbf{r}\,|\,G_s(\nu)\,|\,\mathbf{r}'\rangle$ are unknown. In the domain of the linear hydrogenic Stark effect, the hydrogenic states $|\,n,f,g\,\rangle$ whose wave functions $\langle\mathbf{r}\,|\,n,f,g\,\rangle$ are separable in parabolic coordinates, remain approximate eigenstates of the Coulomb-Stark Hamiltonian with shifted eigenvalues,

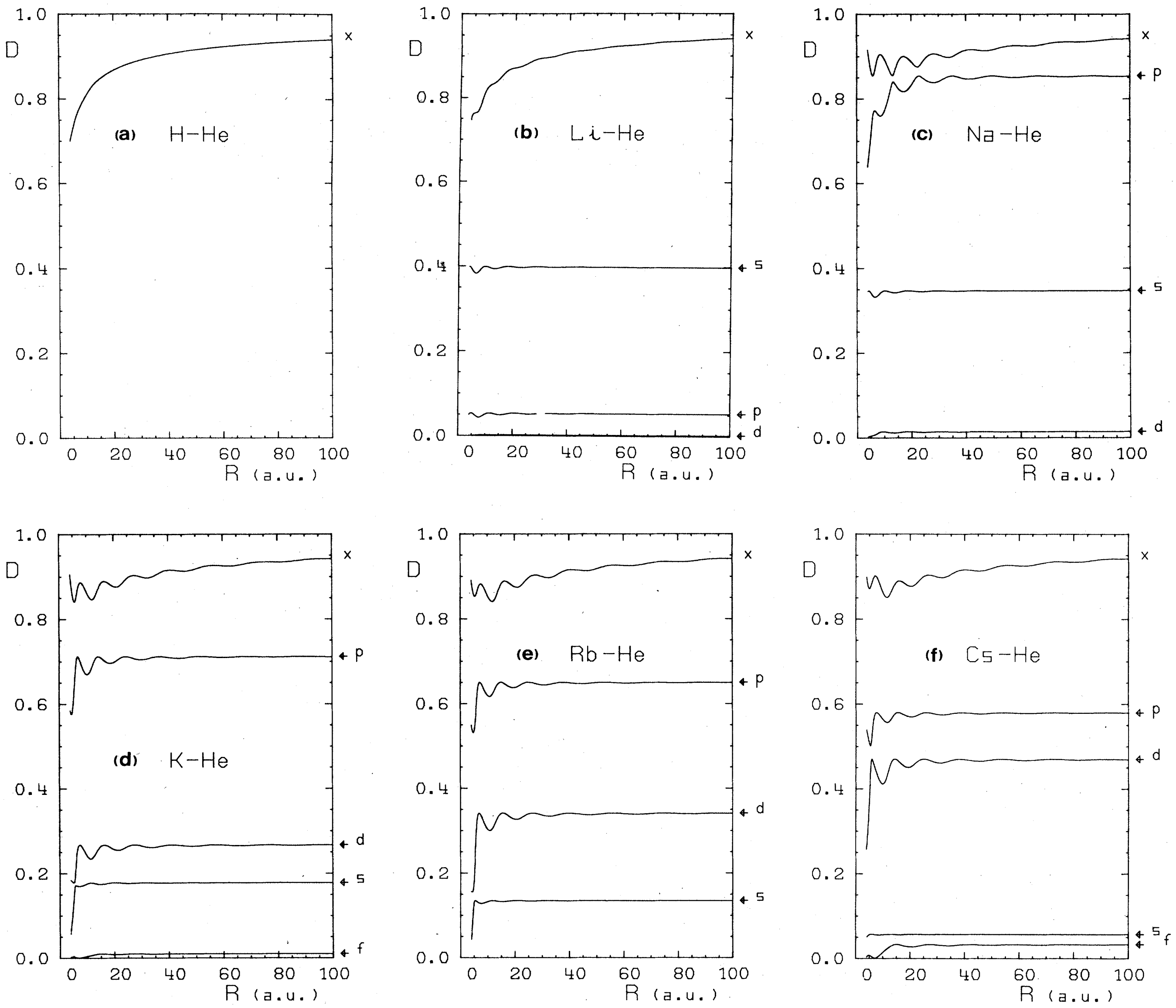

FIG. 4. Fractional part $D(R)$ of the adiabatic Σ quantum defects for alkali-metal—He system computed from Eqs. (24a), (26a), (26b), and (24d). $R \lesssim 2\nu$ (see text).

$$(p^2/2-1/r+\mathcal{E}z)\,|\,n,f,g\,\rangle \simeq [-1/(2n^2)+\tfrac{3}{2}n(f-g)\mathcal{E}]\,|\,n,f,g\,\rangle\,, \qquad (32)$$

where

$$|\,n,f,g\,\rangle=\sum_{l}|\,n,l,m\,\rangle\langle\, l,m\,|\,FfFg\,\rangle\,. \qquad (33)$$

The value of F in the Clebsch-Gordan coefficients of Eq. (33) is $(n-1)/2$. This suggests the following approximation for $G_s(\nu)$:

$$G_s(\nu)\simeq G(\nu)+\sum_{f,g}|\,n,f,g\,\rangle\langle\, n,f,g\,|\,b(\nu,n,f,g) \qquad (34)$$

with n the closest integer to ν and $b(\nu,n,f,g)$ the following difference:

$$b(\nu,n,f,g)=[-1/(2\nu^2)+(1/2n^2)-\tfrac{3}{2}n(f-g)\mathcal{E}]^{-1} -[-1/(2\nu^2)+1/(2n^2)]^{-1}\,. \qquad (35)$$

It is seen that the Coulomb-Stark Green function $\langle\,\mathbf{r}'\,|\,G_s(\nu)\,|\,\mathbf{r}\,\rangle$ has, within this approximation, the correct divergent behaviors for the limiting cases $\mathbf{r}'\rightarrow\mathbf{r}$ (ν fixed) and $(-1/2\nu^2)\rightarrow -1/2n^2+\tfrac{3}{2}n(f-g)\mathcal{E}$ ($\mathbf{r}',\mathbf{r}$ fixed). For $\nu\rightarrow n$, it diverges only if $f-g=0$ as should be the case. It will be seen later on that this approximation is essentially equivalent to a result previously obtained by Harmin[25] for the determination of the Stark spectra of alkali-metal atoms [$V_p=0$ in Eq. (28)].

Among the eigenvalues of H [Eqs. (28)], those, to be denoted $-1/(2\nu^2)$, which are different from

$-1/(2n^2)+\frac{3}{2}n(f-g)\mathscr{E}$, are easily shown to be solutions of

$$\det\mathscr{A}=0 \tag{36a}$$

with $\mathscr{A}$ a Hermitian matrix defined by

$$\mathscr{A}_{11}=\langle\xi\,|\,e^{i\theta L_y}G_s(\nu)e^{-i\theta L_y}\,|\,\xi\rangle-1/\alpha\ , \tag{36b}$$

$$\mathscr{A}_{1,2+l^2+l+m}=\langle\xi\,|\,e^{i\theta L_y}G_s(\nu)r_l^{3/2}\,|\,r_l,l,m\,\rangle =\mathscr{A}^{*}_{2+l^2+l+m,1}\ , \tag{36c}$$

$$\mathscr{A}_{2+l'^2+l'+m,2+l^2+l+m} =r_{l'}^{3/2}r_l^{3/2}\langle r_{l'},l',m\,|\,G_s(\nu)\,|\,r_l,l,m\,\rangle-\delta_{ll'}/a_l\ , \tag{36d}$$

all other matrix elements being equal to zero. $1+l^2+l+m$ corresponds to the position of $|\,r_l,l,m\,\rangle$ if the set of $|\,r_l,l,m\,\rangle$ is ordered according to increasing l values, and for fixed l increasing m values.

At this stage it is of interest to look at the symmetry properties of $\mathscr{A}$. If Π denotes the parity operator, $\Pi\exp(-i\pi L_y)$ corresponds to a reflection through the xz plane. As G_s commutes with $\Pi\exp(-i\pi L_y)$, and as

$$\exp(-i\pi L_y)\,|\,l,m\,\rangle=(-1)^{l-m}\,|\,l,-m\,\rangle\ , \tag{37}$$

$$\Pi\,|\,l,m\,\rangle=(-1)^l\,|\,l,m\,\rangle\ , \tag{38}$$

one obtains

$$\langle r_{l'},l',m\,|\,G_s(\nu)\,|\,r_l,l,m\,\rangle =\langle r_{l'},l',-m\,|\,G_s(\nu)\,|\,r_l,l,-m\,\rangle\ . \tag{39}$$

Using the relation

$$\langle\,l,m'\,|\exp(-i\theta L_y)\,|\,l,m\,\rangle \equiv d^l_{m'm}(\theta)=(-1)^{m'-m}d^l_{-m',-m}(\theta)\ , \tag{40}$$

one also obtains

$$\langle\xi\,|\exp(i\theta L_y)G_s(\nu)\,|\,r_l,l,m\,\rangle =(-1)^m\langle\xi\,|\exp(i\theta L_y)G_s(\nu)\,|\,r_l,l,-m\,\rangle\ . \tag{41}$$

Finally, as G_s commutes with L_z, a change of basis corresponding to ordering the set $|\,r_l,l,m\,\rangle$ in order of increasing m values, and for fixed m increasing l values leads $\mathscr{A}$ to be block diagonalized.

For $r\lesssim 2n$ the radial part $R_{nl}(r)$ of $\langle\,\mathbf{r}\,|\,n,l,m\,\rangle$ satisfies

$$R_{n,l}(r)\simeq c(n,l)J_{2l+1}(\sqrt{8r}\,)/\sqrt{r}\ , \tag{42a}$$

$$c(n,l)=(-1)^{n-l-1}\sqrt{2}n^{-l-2} \times[(n+l)!/(n-l-1)!]^{1/2}\ . \tag{42b}$$

Then, a tedious but elementary calculation analogous to that of Sec. II B shows that the condition $\det\mathscr{A}=0$ reduces to

$$\det\wp=0 \tag{43a}$$

with

$$\wp_{11}=P_{11}+2\pi\sum_{f,g}|\,\langle\,\mathbf{R}\,|\,n,f,g\,\rangle\,|^2 b(\nu,n,f,g)\ , \tag{43b}$$

$$\wp_{1,2+l^2+l+m}=d^l_{m0}(\theta)P_{1,l+2} +c(n,l)\sum_{f,g}\langle FfFg\,|\,lm\,\rangle\langle\,\mathbf{R}\,|\,n,f,g\,\rangle \times b(\nu,n,f,g)\ , \tag{43c}$$

$$\wp_{2+l'^2+l'+m,2+l^2+l+m} =\delta_{ll'}P_{l+2,l+2}+(-1)^{l'+l}(\pi n^3)^{-1} \times\sum_{f,g}\langle\,l'm\,|\,FfFg\,\rangle\langle FfFg\,|\,lm\,\rangle b(\nu,n,f,g)\ , \tag{43d}$$

all other matrix elements being equal to zero. Two particular cases of the preceding result are now considered.

First, if $V_\rho=0$ in Eq. (28), the physical problem reduces to the Stark spectrum of alkali-metal atoms. For a given value of m, the Eq. (43a) reduces to

$$\det B=0 \tag{44a}$$

with

$$B_{l'+1,l+1}=\wp_{2+l'^2+l'+m,2+l^2+l+m}\ . \tag{44b}$$

Eqs. (44) are essentially equivalent to a result previously obtained by Harmin [see Eqs. (2.15′), (2.11), (3.4), and (3.5) of Ref. 25]. Results obtained by solving Eqs. (44) for Na, $m=0$, $n=10$, $\mathscr{E}=2\,000$ V/cm are reported in column 3 of Table I. Column 2 reports the results obtained according to the very accurate method of Zimmerman *et al.*[24] using 43 basis vectors for diagonalization of the Hamiltonian. The comparison is good. The largest differences are for the first and last line which correlate, as $\mathscr{E}\rightarrow 0$, to the nonhydrogenic $11p$ and $11s$ level, respectively. Column 1 displays the hydrogenic values according to first-order perturbation theory [Eq. (32)] for comparison.

The second particular case now considered is H-He, $n=10$, and $\mathscr{E}=2\,000$ V/cm. Equation (43a) reduces here to $\wp_{11}=0$, as all V_l are zero. The unnormalized eigen-

TABLE I. Na Stark spectrum for $n=10$, $m=0$, $\mathscr{E}=2\,000$ V/cm. Units are cm^{-1}. Column I. Hydrogenic energies to first-order perturbation theory [see Eq. (32), and multiply by the reduced mass Na$^+$ e$^-$ expressed in a.u.]. Column II: Na stark spectrum computed according to the method of Zimmerman *et al.* (Ref. 24). Column III: Na Stark spectrum computed according to Eqs. (44).

I	II	III
1085.82	1064.91	1064.69
1088.38	1087.53	1087.51
1090.94	1090.60	1090.58
1093.51	1093.56	1093.54
1096.07	1096.47	1096.46
1098.63	1099.37	1099.36
1101.19	1102.27	1102.26
1103.75	1105.18	1105.18
1106.31	1108.15	1108.17
1108.87	1178.22	1177.95

states associated with the roots ν are $G_s(\nu)\exp(-i\theta L_y)\,|\,\xi\rangle$. These states remain invariant by reflection though the plane containing z and the internuclear axis,

$$\begin{aligned}\exp(-i\pi L_y)\Pi G_s(\nu)\exp(-i\theta L_y)\exp(-iR\hat{\mathbf{z}}\cdot\mathbf{p})\,|\,\rho,0,0\rangle\\ =G_s(\nu)\exp[-i(\theta+\pi)L_y]\exp(iR\hat{\mathbf{z}}\cdot\mathbf{p})\Pi\,|\,\rho,0,0\rangle\\ =G_s(\nu)\exp(-i\theta L_y)\exp(-iR\hat{\mathbf{z}}\cdot\mathbf{p})\,|\,\rho,0,0\rangle\ .\end{aligned}\tag{45}$$

These states are then denoted A' in usual spectroscopic notations. All states A'' which change sign under the reflection remain unperturbated. For $\theta=0$ or π, the problem still has rotational symmetry along the internuclear axis, and the perturbed states are Σ states, a particular case of A' states.

Results for $\theta=0,\pi,\pi/2$ are presented in Figs. 5(a)–5(c), respectively. For $\theta=0$, it is seen that the lowest excited levels remain practically unaffected by the presence of helium, except at small internuclear distances. The interpretation of this fact is clear; the hydrogenic states with the lowest excitation energy ($E\leq 1\,100$ cm^{-1}) also have their wave functions essentially localized in the direction $z<0$, i.e., in the direction opposite to that of He. The highest excited levels, to the contrary, are seen to be strongly perturbed by He. For $\theta=\pi$ the situation is reversed. The lowest excited levels are strongly perturbed by He. A series of avoided crossings occurs as the degree of excitation raises and R decreases. The most excited state is then strongly repelled at the top of Fig. 5(b) for $R\lesssim 75$ a.u. For $\theta=\pi/2$, the perturbed levels not only correlate to the $n=10$ hydrogenic Stark levels with $m=0$, but also with the all 19 $(2n-1)$ of the hydrogenic Stark levels. The states which are perturbed for all R values are then those near the middle, i.e., those with energy close to $-1/2n^2$, whose wave functions cover appreciably both domains $z<0$, $z>0$. Finally, Fig. 6 shows the angular dependence for a particular value of R ($R=50$ a.u.).

V. DISCUSSION AND CONCLUSION

The first point to be discussed now concerns the $\Pi,\Delta,\ldots$ or A'' adiabatic energy levels. They remain unaffected in the present approach as only the s wave relative to the rare gas is taken into account. A classical argument shows that these levels should indeed be less sensitive to the presence of the rare gas except at small internuclear distances. From a classical point of view, the angular momentum of the Rydberg electron located at a point x, at a perpendicular distance a from the internuclear axis, is, relative to this axis, less than or equal to (ap_x). It is therefore less than unity, except for x small, as the e^-—rare-gas interaction is essentially short ranged and p_x [Eq. (11)] decreases for increasing x.

The second point to be discussed concerns the applications of the present work to collisional processes. Adiabatic energy levels are relevant for describing a collision if the Born-Oppenheimer approximation holds. This requires typically $n\lesssim 12$ for thermal collisions but higher n values are also relevant for subthermal collisions. Computing the dynamical couplings in the Born-Oppenheimer approximation requires the knowledge of the adiabatic electronic wave functions. It will now briefly be discussed how these functions could be approximated within the present framework. The case of zero external electric field is considered for the sake of simplicity but generalization to the case where a small external electric field is present is straightforward. The (unnormalized) eigenstate

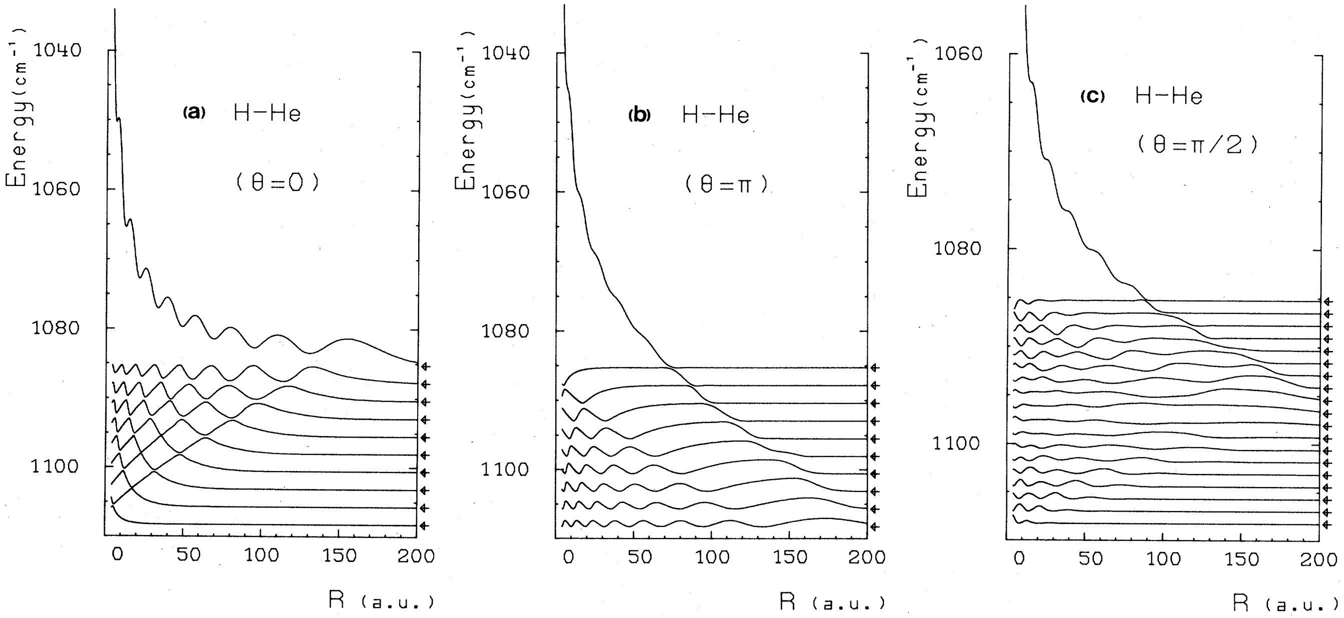

FIG. 5. Adiabatic ionization energies for the H-He system in the presence of an electric field $\mathscr{E}$, computed from Eqs. (43). $n=10$, $\mathscr{E}=2\,000$ V/cm, θ is the angle between $\mathscr{E}$ and the internuclear axis H-He oriented from H$^+$ to He. The arrows correspond to the atomic hydrogenic energy levels computed to first-order Stark perturbation [Eq. (32)].

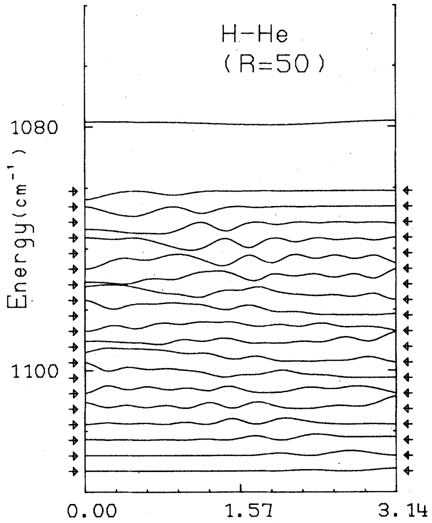

FIG. 6. As in Fig. 5, but R fixed ($R=50$) and θ in abscissa.

$|\psi\rangle$ of the Hamiltonian H of Eq. (1) associated to an eigenvalue $-1/(2\nu^2)$, ν not an integer, can be obtained from the Coulomb Green operator [Eq. (5a)] as

$$|\psi\rangle = G(\nu)\{\, |\xi\rangle\alpha\langle\xi|\psi\rangle + \sum_{l,m} |r_l,l,m\rangle a_l r_l^3 \langle r_l,l,m|\psi\rangle\} \,.$$

Projection of this equation on $\langle\xi|$ and on the $\langle r_l,l,m|$ not only provides the values of ν [see Eq. (24)] but also the ratios $\langle\xi|\psi\rangle/\langle r_l,l,m|\psi\rangle$, $\langle r_l,l,m|\psi\rangle/\langle r_{l'},l',m'|\psi\rangle$. Therefore, approximate adiabatic electronic wave functions $\langle \mathbf{r}|\psi\rangle$ can be determined once α,ρ,a_l,r_l are known. Equation (6) and (22) provide a relation between α and ρ, and between the a_l and r_l values. The knowledge of the wave functions therefore requires ρ and the r_l to be fitted so that Eqs. (6) and (22) are satisfied when varying p and n, respectively. However, such a requirement may be difficult to fulfill when large polarization effects are involved.

To conclude, the Green-function approach provides a very convenient way for computing adiabatic electronic energy levels for Rydberg alkali-metal—light-rare-gas systems directly from the knowledge of physical atomic data (quantum defects and s-wave scattering phase shifts). Pseudopotential or model-potential calculations already provide a great simplification when compared to the *ab initio* calculations. We would like to emphasize that the Green-function method is still much more simple, since it avoids the construction of pseudopotentials or model potentials. For low excited states, *ab initio*, pseudopotential or model-potential calculations remain necessary and provide an interesting test of the present approach. For very excited levels, the Green-function approach seems to be the only tractable method. It has, moreover, the advantage of flexibility as exemplified by the possibility of taking into account the influence of a small electric field. Finally this method allows one to understand how nonhydrogenic systems are simply related to the Coulomb problem.

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APPENDIX: BESSEL FUNCTIONS AS LIMITING CASES OF WHITTAKER FUNCTIONS

The first-order term of the expansion of $\mathcal{M}_{\nu,\mu/2}$ in terms of Bessel functions [see Eq. (16) of Sec. 7 of Ref. 19] yields

$$\mathcal{M}_{\nu,l+1/2}(2r/\nu) \simeq \nu^{-l-1}\sqrt{2r}\,J_{2l+1}(\sqrt{8r}\,) \,. \tag{A1}$$

This approximation requires $r \lesssim 2\nu$.

Using the definition of $W_{\nu,\mu/2}$ in terms of $\mathcal{M}_{\nu,\mu/2}$ and $\mathcal{M}_{\nu,-\mu/2}$ [see Eq. (18a) of Sec. 2 of Ref. 19], together with the relation $\Gamma(z)\Gamma(1-z)=\pi/\sin(\pi z)$ one then obtains

$$\begin{aligned} W_{\nu,\mu/2}(2r/\nu) \simeq [\sqrt{2r}\,/\sin(\pi\nu)][\, & -\nu^{-(\mu+1)/2}\Gamma(\nu+(\mu+1)/2)\sin\{\pi[\nu+(\mu+1)/2]\}J_{\mu}(\sqrt{8r}\,) \\ & +\nu^{(\mu-1)/2}\Gamma(\nu+(1-\mu)/2)\sin\{\pi[\nu+(1-\mu)/2]\}J_{-\mu}(\sqrt{8r}\,)] \,. \end{aligned} \tag{A2}$$

Now if $\mu/(2\nu) \ll 1$,

$$\nu^{-(\mu+1)/2}\Gamma(\nu+(\mu+1)/2) \simeq \Gamma(\nu) \simeq \nu^{(\mu-1)/2}\Gamma(\nu+(1-\mu)/2) \,.$$

Recalling the definition of Y_μ in terms of J_μ and $J_{-\mu}$ [see Eq. (9.1.2) of Ref. 20], one obtains

$$\begin{aligned} W_{\nu,l+1/2}(2r/\nu) & \\ \simeq -\Gamma(\nu)\sqrt{2r}\, & \{\sin[\pi(\nu-l)]Y_{2l+1}(\sqrt{8r}\,) \\ & +\cos[\pi(\nu-l)]J_{2l+1}(\sqrt{8r}\,)\} \,. \end{aligned} \tag{A3}$$

This approximation requires both $r \lesssim 2\nu$ and $l/\nu \ll 1$.

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