Complete Feshbach-type calculations of energy positions and widths of autoionizing states in Li-like atoms

Juan Carlos Cardona,[1] José Luis Sanz-Vicario,[1,*] and Fernando Martín[2]

[1]*Grupo de Física Atómica y Molecular, Instituto de Física, Universidad de Antioquia, Medellín, Colombia*
[2]*Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

Applications of the Feshbach formalism to systems of more than two active electrons are very scarce due to practical limitations in the construction of the projection operators $\mathcal{P}$ and $\mathcal{Q}$ that are inherent to the theory. As a consequence, most previous applications rely on the use of approximate quasiprojection operators, whose theoretical justification is not yet clear. In this work, an implementation of the Feshbach formalism for three-electron atoms is presented that includes all the ingredients of the original formalism. Energy positions and autoionization widths of the lowest $^2S^e$, $^2P^o$, and $^2D^e$ autoionizing states of Li and Ne^{7+} have been evaluated. The results show that the use of quasiprojection operators is justified for the evaluation of resonant positions. However, for the $^2S^e$ states of Li, the use of quasiprojection operators can lead to errors in the autoionization widths of the order of 100%.

I. INTRODUCTION

Recent advances in the generation of subfemtosecond laser pulses and subsequently in attosecond metrology have opened up the way to photodynamical studies of short-living metastable states at the atomic time scale. Probing with attosecond pulses has revealed the excitation and relaxation dynamics of core-excited atoms [1,2] and more specifically the time-evolution of autoionizing states [3]. In particular, ultrafast probing of localization of inner holes in molecules is receiving a great deal of attention [4]. These advances call for theoretical methods that can provide an accurate description of autoionizing states in many-electron atoms in both stationary and dynamical pictures.

Among these, the Feshbach projection-operator formalism [5] has been successfully used in the past to evaluate resonance parameters of two-electron systems (see, e.g., [6,7] and references therein). This method provides a rigorous procedure for decomposing the total wave function into its resonant and nonresonant parts through the use of $\mathcal{Q}$ and $\mathcal{P}$ orthogonal projection operators. However, the explicit construction of these operators for systems with three or more electrons poses practical difficulties. Thus, prescriptions based on the use of quasiprojectors have been derived and applied by relaxing the idempotency condition inherent in true projection operators [6,8–13]. Procedures for separating the resonant and nonresonant components of the scattering wave function without explicit use of Feshbach projectors have also been proposed [14,15], with some reported results for He$^-$ [16], but their applicability to three or more electron systems depends very much on the specific atom under consideration.

Alternatively, the saddle-point method proposed by Chung [17] has proven to be effective and accurate to evaluate resonance positions in two- and three-electron systems with one or more holes in the inner shells. These holes are built directly into the variational wave function [18] through

hole-projection operators. In spite of this success, results for autoionization widths are still very scarce. Also, a rigorous foundation of the method is missing, which has led to some controversy [19–22].

At variance, complex scaling methods remain in general valid without considerable restrictions when applied to many-electron atomic systems. In this method, all radial coordinates are rotated in the complex plane through the transformation $r_i \rightarrow r_i e^{i\theta}$, where θ is the rotation angle. In this way, energy positions E_s, which directly include the correction due to the energy shift (see the following), and widths Γ_s are directly obtained from the real and imaginary parts of complex eigenvalues associated with a generalized complex symmetric eigenvalue problem; that is, $E = E_s + i\Gamma_s/2$. This approach has been used by many authors (for reviews on the subject, see [23–25]) and more recently by one of us to calculate resonance positions and widths, as well as the photodetachment spectra of three-(active)-electron negative ions like He$^-$ [26], Be$^-$ [27], Mg$^-$, and Ca$^-$ [28]. In spite of the huge success of this approach, the performance of this kind of methods in time-dependent pictures is still uncertain, at variance with the well established time-dependent close-coupling methods (see, e.g., [29] and new developments in time-dependent *R*-matrix theory [30]) which make explicit use of atomic eigenstates associated with the true (non-complex-rotated) Hamiltonian. In the last few years, time-dependent close-coupling methods that make use of Feshbach states have been shown to be a powerful approach to describing the time evolution of the autoionizing decay in two-electron systems [31]. Therefore, investigations on the applicability of the Feshbach method for obtaining resonance parameters in many-electron systems is the necessary first step before going into the time domain.

The aim of this work is to apply the Feshbach formalism to three-electron atomic systems, essentially without approximations, apart from the obvious one which is truncation of the basis set. As mentioned earlier, most existing approximations are related to the construction of the $\mathcal{P}$ projector, which is precisely the fundamental tool in Feshbach's theory. Feshbach himself [5] provided in his seminal 1962 article a general

---

*sanjose@fisica.udea.edu.co

prescription for building the $\mathcal{P}$ projector. More than 20 years later, Temkin and Bhatia [6,32] proposed the first practical way to construct projection operators for three-electron systems. With the exception of the work of Berk *et al.* [33] on the He$^-$ resonances, we are unaware of published work using the full $\mathcal{P}$ projector. Nevertheless, the results of Berk *et al.* are intriguing since the resonance positions obtained with the full projector compare worse with experiment than those obtained with a quasiprojector in which several terms are removed from $\mathcal{P}$. That is why most calculations for three-electron atomic systems have been performed with quasiprojectors. However, a detailed investigation of the importance of the different terms in the $\mathcal{P}$ projector is still lacking. A first attempt toward this goal in Li-like atoms can be found in Ref. [34], although the reported calculations were performed with the simplest possible description of the remaining ion (a single configuration in terms of pure hydrogenic functions) and with a rather small basis set, so that no relevant conclusion on this particular issue could be obtained.

In this work we have used a computational method that allows us to perform complete Feshbach calculations that include the full projection operators and the optical polarization potential that appears in the rigorous theory. Contributions of the different terms to the energy positions and Auger widths are quantitatively evaluated for Li and Ne^{7+}. The much more correlated He$^-$ system will be the subject of future investigations.

This article is organized as follows. In Sec. II, we present a short description of the Feshbach method and our implementation for three-electron atoms. We will emphasize those aspects related to the construction of the projector operator $\mathcal{P}$. In Sec. III we present our results for energy positions, energy shifts, and widths for the $^2S^e, ^2P^o$, and $^2D^e$ doubly excited states of Li and Ne^{7+} lying below the first excitation threshold of the remaining ions Li$^+$ and Ne^{8+}. We end up with some conclusions in Sec. IV. Atomic units are used throughout unless otherwise stated.

II. THEORY

A. Feshbach projection formalism

We will not dig into all the details of the Feshbach theory, which can be found elsewhere [5,6], but only into those that are of interest in the present work. The foundation of the Feshbach projection-operator formalism stems from the definition of projection operators $\mathcal{P}$ and $\mathcal{Q}$ which split the total wave function into nonresonant scatteringlike $\mathcal{P}\Psi$ and resonant quadratically integrable $\mathcal{Q}\Psi$ parts, such that $\Psi = \mathcal{P}\Psi + \mathcal{Q}\Psi$. These projector operators must satisfy conditions of completeness ($\mathcal{P} + \mathcal{Q} = 1$), idempotency ($\mathcal{P}^2 = \mathcal{P}$ and $\mathcal{Q}^2 = \mathcal{Q}$), and orthogonality ($\mathcal{P}\mathcal{Q} = 0$). The projected wave functions must satisfy the asymptotic boundary conditions $\lim_{r_i \to \infty} \mathcal{P}\Psi = \Psi$ and $\lim_{r_i \to \infty} \mathcal{Q}\Psi = 0$.

Starting from the Schrödinger equation $H\Psi = E\Psi$ and the aforementioned splitting of the total wave function, a formal equation for $\mathcal{P}\Psi$ easily arises,

$$(\mathcal{P}H\mathcal{P} + V_{\text{opt}} - E)\mathcal{P}\Psi = 0, \tag{1}$$

where the nonlocal generalized optical potential V_{opt} reads

$$V_{\text{opt}}(E) = \mathcal{P}H\mathcal{Q}(E - \mathcal{Q}H\mathcal{Q})^{-1}\mathcal{Q}H\mathcal{P}. \tag{2}$$

This optical potential may be expanded in terms of the eigensolutions Φ_n of the projected Hamiltonian $\mathcal{Q}H\mathcal{Q}$:

$$(\mathcal{Q}H\mathcal{Q} - \mathcal{E}_n)\Phi_n = 0, \tag{3}$$

where the $\mathcal{E}_n$ eigenvalues are close to the true resonance energies.

For an energy $E \sim \mathcal{E}_s$ (close to an isolated resonant state s) the optical potential may be separated into two components,

$$V_{\text{opt}}(E) = V_{\text{opt}}^s(E) + V_{\text{opt}}^{n \neq s}(E) = \mathcal{P}H\mathcal{Q}\frac{|\Phi_s\rangle\langle\Phi_s|}{E - \mathcal{E}_s}\mathcal{Q}H\mathcal{P}$$
$$+ \sum_{n \neq s} \mathcal{P}H\mathcal{Q}\frac{|\Phi_n\rangle\langle\Phi_n|}{E - \mathcal{E}_n}\mathcal{Q}H\mathcal{P}, \tag{4}$$

so that Eq. (1) for $\mathcal{P}\Psi$ can now be written in the form

$$(\mathcal{P}H'\mathcal{P} - E)\mathcal{P}\Psi = -V_{\text{opt}}^s\mathcal{P}\Psi, \tag{5}$$

with

$$H' = H + V_{\text{opt}}^{n \neq s}. \tag{6}$$

A formal solution to Eq. (5) can be written by using the Lippman-Schwinger equation in terms of the solution $\mathcal{P}\Psi^0$ of its related homogeneous scattering equation (nonresonant continuum),

$$(\mathcal{P}H'\mathcal{P} - E)\mathcal{P}\Psi^0 = 0, \tag{7}$$

and the Green function,

$$G_P^s(E) = \text{P}\left(\frac{1}{E - \mathcal{P}H'\mathcal{P}}\right) + i\pi\delta(E - \mathcal{P}H'\mathcal{P}), \tag{8}$$

where P stands for the Cauchy principal value. In this way, the solution $\mathcal{P}\Psi$ resulting from Eq. (5) reads

$$\mathcal{P}\Psi = \mathcal{P}\Psi^0 + G_P^s(E)$$
$$\times \frac{\mathcal{P}H\mathcal{Q}|\Phi_s\rangle\langle\Phi_s|\mathcal{Q}H\mathcal{P}|\mathcal{P}\Psi^0\rangle}{E - \mathcal{E}_s - \langle\Phi_s|\mathcal{Q}H\mathcal{P}G_P^s(E)\mathcal{P}H\mathcal{Q}|\Phi_s\rangle}. \tag{9}$$

The resonant contribution to the electronic continuum comes from the second term of the latter equation. In the vicinity of the s resonance, this contribution has a total width Γ_s given by

$$\Gamma_s = 2\pi\langle\Phi_s|\mathcal{Q}H\mathcal{P}\delta(E_s - \mathcal{P}H'\mathcal{P})\mathcal{P}H\mathcal{Q}|\Phi_s\rangle \tag{10}$$

and is centered at an energy $E = \mathcal{E}_s + \Delta_s$, where Δ_s is an energy shift given by

$$\Delta_s = \langle\Phi_s|\mathcal{Q}H\mathcal{P}\,\text{P}\left(\frac{1}{E_s - \mathcal{P}H'\mathcal{P}}\right)\mathcal{P}H\mathcal{Q}|\Phi_s\rangle. \tag{11}$$

Introducing the resolvent $1/(E - \mathcal{P}H'\mathcal{P})$ written in terms of the eigensolutions of $\mathcal{P}H'\mathcal{P}$, one finally arrives at expressions for the width and the energy shift suitable for computational purposes:

$$\Gamma_s = 2\pi|\langle\Phi_s|\mathcal{Q}H\mathcal{P}|\mathcal{P}\Psi^0(E = E_s)\rangle|^2, \tag{12}$$

$$\Delta_s = \sum_{E' \neq E_s} \int dE' \frac{|\langle\Phi_s|\mathcal{Q}H\mathcal{P}|\mathcal{P}\Psi^0(E')\rangle|^2}{E_s - E'}. \tag{13}$$

As the actual position of the s resonance is $E_s = \mathcal{E}_s + \Delta_s$, the eigenvalues of $\mathcal{Q}H\mathcal{Q}$ are (usually very good) approximations for this position. The nonresonant contribution to the optical potential in the Hamiltonian H', $V_{\text{opt}}^{n \neq s}$ [see Eq. (6)] has been included in previous Feshbach-like calculations for two-electron systems [7] but never for three-electron atoms. It contributes to second order in $\mathcal{Q}H\mathcal{P}$ to $\mathcal{P}\Psi$, to second order to the widths, and to fourth order to the energy shifts. It represents polarization of the two-electron ionic system and is usually small when all resonances lie very far away from each other.

B. Projection operators

As mentioned earlier, in Feshbach theory, the projection operators $\mathcal{P}$ and $\mathcal{Q}$ are not univocally defined but must satisfy specific mathematical conditions. Feshbach [5] and later Temkin and Bhatia [32] proposed a rigorous construction procedure of these operators that is valid for any many-electron atom. For an N-electron system, the complete expression of the $\mathcal{P}$ projector for the case of autoionizing states lying below the first excited state of the ionized system (i.e., below the second ionization threshold) reads [5]

$$\mathcal{P} = \sum_{i=1}^{N} |\psi_0(\mathbf{x}^{(i)})\rangle \left[1 + \sum_{\lambda_\alpha \neq 1} \frac{|v_\alpha(\mathbf{x}_i)\rangle \langle v_\alpha(\mathbf{x}_i)|}{\lambda_\alpha - 1} \right] \langle \psi_0(\mathbf{x}^{(i)})|,$$
(14)

where $\mathbf{x}^{(i)}$ stands for the collection of all coordinates $\mathbf{x}_k = (r_k, \Omega_k, s_k)$ (radial r_k, angular Ω_k, and spin s_k coordinates) for the N electrons ($k = 1, 2, \ldots, N$) with only the coordinate $\mathbf{x}_i$ of the ith electron excluded, ψ_0 corresponds to the (fully antisymmetric) wave function of the ionized atom (hereafter called target wave function), and the $v_\alpha(\mathbf{x}_i)$ one-electron wave functions are the eigensolutions (and λ_α the eigenvalues) of the integral equation

$$v_\alpha(\mathbf{x}_i) = \lambda_\alpha \int K(\mathbf{x}_i, \mathbf{x}_j) v_\alpha(\mathbf{x}_j) d\mathbf{x}_j,$$
(15)

with the kernel function defined as $K(\mathbf{x}_i, \mathbf{x}_j) = N \langle \psi_0(\mathbf{x}^{(i)}) | \psi_0(\mathbf{x}^{(j)}) \rangle$. The intricacies involved in the solution of the latter integral equation for arbitrary expansions of the target wave function has led in most cases to drop the sum over λ_α in Eq. (14). In this work, we solve this equation by expanding the one-electron v_α functions in terms of the very same one-electron basis used to build the target configuration interaction (CI) wave function. The integral equation thus turns into an algebraic eigenvalue problem $(\mathbf{K} \cdot \mathbf{S} - \lambda^{-1}) \cdot \mathbf{C} = 0$ that can be solved straightforwardly.

It has been demonstrated [32] that the preceding form of the projection operator (14) guarantees its idempotency, but only when the operators are computed as matrix elements of antisymmetrized wave functions. Hereafter we frequently use the notation $\mathcal{P} = \mathcal{P}^{(0)} + \Delta\mathcal{P}$ to denote the two terms in the $\mathcal{P}$ projection operator (14). If one removes the second term $\Delta\mathcal{P}$, idempotency is lost and the projector becomes instead a so-called quasiprojector. Almost all calculations carried out with Feshbach-like formalisms in three-electron atoms have made use of quasiprojectors. Neglect of $\Delta\mathcal{P}$ is an approximation that works better as the nuclear charge Z increases, since

this term scales as $\sim 1/Z$. It must be stressed that when a single configuration built upon hydrogenic functions is used to describe the target $1s^2$ state, $\Delta\mathcal{P} = 0$ and $\mathcal{P}$ reduces identically to $\mathcal{P}^{(0)}$, since all λ_α eigenvalues are equal to unity. However, this choice [34] turns out to be a rather poor approximation for the description of the target state.

In this work we use a CI wave function for the target ground state, in which the configurations are built from a basis of Slater-type orbitals (STOs). Berk *et al.* [33] used Hylleraas-type correlated configurations from which they could only obtain an approximate description of $\Delta\mathcal{P}$. They compared results for resonant positions in He$^-$ computed with the complete projector and with the quasiprojector, and, surprisingly, those with the full projector compared worse with the experiment. Unfortunately, energy shifts were not calculated, so it is difficult to say if the origin of the discrepancy is due to the neglect of these energy shifts or to the approximations made to describe $\Delta\mathcal{P}$. With our method we can compute energy shifts very easily and describe $\Delta\mathcal{P}$ very accurately within the same subspace as that used to build the two-electron configurations of the target state.

C. Pseudopotential method

A Phillips-Kleinman pseudopotential approach was introduced by Martín *et al.* [35] as an alternative but equivalent way of solving Eq. (3) that avoids explicit projection of the basis set onto the $\mathcal{Q}$ subspace. In this method, instead of $\mathcal{Q}H\mathcal{Q}$, one uses the effective Hamiltonian H_{eff}:

$$H_{\text{eff}} = H + M\mathcal{P},$$
(16)

where M is a very large number. This Hamiltonian projects upward in energy (up to $E \sim M$, that is, well above the $\mathcal{Q}$ states) all eigenstates associated with the $\mathcal{P}$ subspace. In the limit $M \to \infty$, the solutions obtained for the $\mathcal{Q}$ states are identical to those arising from Eq. (3). The main practical issue with the pseudopotential approach is that partition into $\mathcal{Q}H\mathcal{Q}$ and $\mathcal{P}H\mathcal{P}$ is no longer necessary and the $\mathcal{Q}H\mathcal{Q}$ resonance eigenvalues are directly obtained from the diagonalization of H_{eff} in the CI basis. In this way, explicit projection onto the $\mathcal{Q}$ subspace is avoided and only construction of the $\mathcal{P}$ operator is required. Applications of this method have so far been restricted to one-electron targets [36,37] for which the projector is known exactly. Recently, this pseudopotential approach has been used to compute autoionizing states in Be-like atomic systems in order to remove the unphysical Rydberg series of virtual core states [38].

D. Three-electron calculations

We have implemented a three-electron code [39], following the general approach proposed by Yan and Drake [40], but for uncorrelated radial configurations. The three-electron CI wave function Ψ is expanded in terms of antisymmetrized configurations $\{\omega_n\}_{n=1}^{N_3}$ (N_3 is the number of three-electron configurations), with $\omega_n = \mathcal{A} W_n(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, where $\mathcal{A}$ is the antisymmetrization operator defined as $\mathcal{A} = \sum_{p=1}^{6} \epsilon_p \mathcal{P}^p = (1) - (12) - (13) - (23) + (123) + (132)$. Note that $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ refers to all coordinates (space and spin) of the ith electron. Thus a single configuration may be written as

$\omega_n = \mathcal{A}W_n = \sum_{p=1}^{6} \phi_n^p \chi^p$, where ϕ_n^p and χ^p correspond to a particular permutation of the space coordinate function and the spin function, respectively. For a symmetric spin-independent operator $\mathcal{O}$, the computation of matrix elements between two configurations reduces to calculating some particular integrals. For instance, in the case of spin doublets (the explicit spin function is given in what follows) the matrix element reads $\langle \omega_i | \mathcal{O} | \omega_j \rangle = 12 \mathcal{O}_{ij}^{11} + 12 \mathcal{O}_{ij}^{12} - 6 \mathcal{O}_{ij}^{13} - 6 \mathcal{O}_{ij}^{14} - 6 \mathcal{O}_{ij}^{15} - 6 \mathcal{O}_{ij}^{16}$, where $\mathcal{O}_{ij}^{p'p} = \langle \phi_i^{p'} | \mathcal{O} | \phi_j^{p} \rangle$. Consequently, only one permutation is required in the *bra* configuration. The explicit form of W_n reads

$$W_n(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = R_n(r_1, r_2, r_3) \cdot \mathcal{Y}_{LM_L}^{(\ell_1, \ell_2)\ell_{12}, \ell_3}(\Omega_1, \Omega_2, \Omega_3)$$
$$\cdot \chi^{S,M_S}(s_1, s_2, s_3), \qquad (17)$$

where the radial part is a product of STOs, $R_n(r_1, r_2, r_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}$ (which allows for analytical evaluation of all radial integrals), and the coupled angular part is given by

$$\mathcal{Y}_{LM_L}^{(\ell_1, \ell_2)\ell_{12}, \ell_3}(\Omega_1, \Omega_2, \Omega_3)$$
$$= (-)^{\ell_1 - \ell_2 + m_{12} + \ell_{12} - \ell_3 + M}[\ell_{12}, L]^{1/2}$$
$$\times \sum_{all\ m_i} \begin{pmatrix} \ell_1 & \ell_2 & \ell_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix} \begin{pmatrix} \ell_{12} & \ell_3 & L \\ m_{12} & m_3 & -M \end{pmatrix}$$
$$\times \mathcal{Y}_{\ell_1, m_1}(\Omega_1) \mathcal{Y}_{\ell_2, m_2}(\Omega_2) \mathcal{Y}_{\ell_3, m_3}(\Omega_3). \qquad (18)$$

In Eq. (17) the label n represents all indexes associated with a single configuration; that is, $n \equiv \{j_1(n), j_2(n), j_3(n), \alpha_n, \beta_n, \gamma_n, \ell_1, \ell_2, \ell_3\}$. In this work, we only consider spin doublets and, consequently, we only use one spin eigenfunction associated with this symmetry, namely, $\chi^{1/2, 1/2}(s_1, s_2, s_3) = \alpha(s_1)\beta(s_2)\alpha(s_3) - \beta(s_1)\alpha(s_2)\alpha(s_3)$. This suffices to achieve convergence in large CI expansions [41]. All angular integrals are analytical and were evaluated using graphical methods for angular momentum [42]. We do not include relativistic corrections since they are expected to be negligible for the light ions considered in this work ($Z = 3$–10).

E. Construction of $M\mathcal{P}$ matrix elements

As discussed in Sec. II B the correct Feshbach projector contains two parts. We may restrict our projection operator $\mathcal{P}$ to the first term in Eq. (14), that is, a quasiprojector $\mathcal{P}^0$, or to include additionally the second term, $\mathcal{P}^0 + \Delta\mathcal{P}$. In both cases, the target wave function ψ_0 is computed in terms of a two-electron CI expansion with components $\{\varphi_n\}_{n=1}^{N_2}$ (N_2 is the number of two-electron configurations), where $\varphi_n = \mathcal{A}U_n(\mathbf{x}_1, \mathbf{x}_2)$ and U_n is given by

$$U_n(\mathbf{x}_1, \mathbf{x}_2) = S_n(r_1, r_2) \mathcal{Y}_{\ell_{12} m_{12}}^{(\ell_1, \ell_2)\ell_{12}}(\Omega_1, \Omega_2) \chi^{S,M_S}(s_1, s_2), \qquad (19)$$

with $S_n(r_1, r_2) = r_1^{j_1} r_2^{j_2} e^{-\alpha r_1 - \beta r_2}$ and the angular part may be deduced from Eq. (18). The second term in the projection operator poses no difficulties since we use the same STO basis to build the $\{S_n\}_{n=1}^{N_2}$ configurations and the one-electron v_α functions.

In calculating the matrix elements for $\mathcal{P}$ we use the fact that $[\mathcal{P}, \mathcal{A}] = 0$ and consequently one arrives at the identity

$\langle \omega_i | \mathcal{P} | \omega_j \rangle = \langle \mathcal{P}W_i | \mathcal{A}W_j \rangle$. Thus, it is sufficient to apply the antisymmetrizer on the *ket* and the projector $\mathcal{P}$ on the *bra*, both onto nonantisymmetrized functions W_n, which results very convenient for computational purposes. After spin projection for each permutation, projection onto the correct angular momentum components by using graphical techniques is straightforward. The radial functions S_n are chosen again as STOs, so that all radial integrals in the projection are analytical, as described in [38,43].

F. Building the $\mathcal{P}$ subspace

To construct the nonresonant $\mathcal{P}$ subspace, we solve Eq. (7) in a basis of configurations that is orthogonal to the $\mathcal{Q}$ subspace. This basis contains configurations of the form

$$\varpi_k(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \mathcal{A}(\psi_0(\mathbf{x}^{(3)})v_k(\mathbf{x}_3)), \qquad (20)$$

where $\psi_0(\mathbf{x}^{(3)})$ (using the notation $\mathbf{x}^{(i)}$ introduced in Sec. II B) is the target eigenfunction that was used to build the projection operator $\mathcal{P}$ and $v_k(\mathbf{x}_3) = r_3^{j_k + \ell_3} e^{-\gamma_k r_3} \mathcal{Y}_{\ell_3, m_3}(\Omega_3)\alpha(s_3)$ corresponds to a set of single-electron STO functions (its size is N_1) with the appropriate angular and spin symmetries representing a third electron attached to the target. Diagonalization of the H' Hamiltonian in this basis leads to states that approximately represent the Rydberg series and the continuum states of the three-electron atom. Since the basis is finite, the continuum is discretized and a finite number of energies $\{E_n\}_{n=1}^{N_1}$ and eigenfunctions $\{\mathcal{P}\Psi_{E_n}^0\}$ are obtained. The latter are normalized to unity, while the proper continuum states must be normalized to the Dirac δ. The correct normalization is achieved by multiplying the calculated continuum wave function by the density of states $\rho(E_n) \sim 2/(E_{n+1} - E_{n-1})$ [44]. Hence, the correct expression for the width in terms of the calculated wave functions is

$$\Gamma_s = 2\pi\rho(E_n = \mathcal{E}_s) \left| \langle \Phi_s | \mathcal{Q}H\mathcal{P} | \mathcal{P}\Psi_{E_n = \mathcal{E}_s}^0 \rangle \right|^2. \qquad (21)$$

In general, none of the calculated $\mathcal{P}H'\mathcal{P}$ eigenvalues will match a given resonance energy $\mathcal{E}_s$. To satisfy the resonance condition $E_n = \mathcal{E}_s$, we use an inverse interpolation method [45] that basically consists of slightly modifying the exponents of the STO basis set used to describe the third electron through a common scaling factor. Since the variation of the continuum energies against the scaling parameter ξ is smooth, the interpolation is quite efficient in finding a critical value ξ_c such that one of the continuum discretized eigenvalues satisfies the matching condition $E_n(\xi_c) = \mathcal{E}_s$. Only then is the corresponding continuum eigenfunction $\mathcal{P}\Psi_{E_n = \mathcal{E}_s}^0$ introduced in Eq. (21).

III. RESULTS AND DISCUSSION

We have computed energy positions, energy shifts, and Auger widths of the core-excited autoionizing states of Li and Ne^{7+} located below the second ionization threshold. The different approximations that have been made in earlier calculations work differently for both systems due to the different role played by electron correlation in the representation of the wave functions and the projection operator $\mathcal{P}$. We restrict our study to angular symmetries $^2S^e$, $^2P^o$, and $^2D^e$ for which theoretical and a few experimental results are available.

TABLE I. Energies, widths, and energy shifts for $^2S^e$ resonances of Li below the Li$^+$ $1s2s$ ^3S threshold located at $\sim -5.110\,86$ a.u.. Convergence of resonance parameters for the lowest 11 $^2S^e$ states (using 9740 configurations in $\mathcal{Q}$ space) is shown for different expansions of the quasiprojector $\mathcal{P}^0$, from one-term (closed-shell) to several CI expansions of the target (10, 20, 30, and 40). The last two columns correspond, respectively, to adding $\Delta\mathcal{P}$ (full projector) and the latter plus 40 terms in the optical polarization potential $V_{\mathrm{opt}}^{n\neq s}$. Numbers between parentheses mean powers of 10; that is, $x(a) = x \times 10^a$.

| | Quasiprojector $\mathcal{P}^0$ | | | | | $+\Delta\mathcal{P}$ | $+\Delta\mathcal{P}\,\&\,V_{\mathrm{opt}}$ |
	1	10	20	30	40	40	40
				Energy $\mathcal{E}_s$			
1	−5.407 432	−5.393 348	−5.399 921	−5.399 861	−5.399 854	−5.399 711	−5.399 711
2	−5.200 077	−5.197 824	−5.199 368	−5.199 346	−5.199 343	−5.199 333	−5.199 333
3	−5.157 246	−5.157 244	−5.156 682	−5.156 718	−5.156 723	−5.156 723	−5.156 723
4	−5.150 832	−5.149 689	−5.148 183	−5.148 278	−5.148 291	−5.148 237	−5.148 237
5	−5.143 909	−5.140 838	−5.141 064	−5.141 076	−5.141 078	−5.140 977	−5.140 977
6	−5.135 989	−5.135 163	−5.135 388	−5.135 394	−5.135 395	−5.135 389	−5.135 389
7	−5.127 076	−5.126 754	−5.126 893	−5.126 893	−5.126 893	−5.126 891	−5.126 891
8	−5.121 354	−5.121 229	−5.121 291	−5.121 290	−5.121 290	−5.121 290	−5.121 290
9	−5.117 357	−5.117 316	−5.117 337	−5.117 337	−5.117 337	−5.117 337	−5.117 337
10	−5.114 617	−5.114 602	−5.114 610	−5.114 610	−5.114 610	−5.114 610	−5.114 610
11	−5.112 666	−5.112 659	−5.112 662	−5.112 662	−5.112 662	−5.112 662	−5.112 662
				Width Γ_s			
1	1.219 636(−3)	3.140 223(−3)	2.530 501(−3)	2.535 945(−3)	2.533 445(−3)	2.533 184(−3)	2.558 364(−3)
2	2.510 337(−4)	5.204 214(−4)	3.919 277(−4)	3.955 406(−4)	3.956 074(−4)	3.960 473(−4)	3.999 220(−4)
3	7.292 964(−5)	7.353 528(−5)	2.662 248(−5)	2.729 574(−5)	2.740 224(−5)	2.733 448(−5)	2.226 770(−5)
4	5.476 426(−6)	4.117 884(−5)	8.025 546(−5)	7.949 541(−5)	7.920 005(−5)	8.179 077(−5)	1.087 680(−4)
5	1.064 434(−4)	1.825 391(−4)	2.095 890(−4)	2.081 916(−4)	2.077 350(−4)	2.038 979(−4)	2.056 092(−4)
6	4.734 551(−5)	1.652 718(−4)	1.654 927(−4)	1.639 553(−4)	1.635 326(−4)	1.634 554(−4)	1.524 937(−4)
7	2.267 713(−5)	6.727 902(−5)	5.988 366(−5)	5.974 428(−5)	5.965 103(−5)	5.957 545(−5)	5.658 184(−5)
8	9.298 445(−6)	2.693 569(−5)	2.237 465(−5)	2.239 494(−5)	2.237 043(−5)	2.234 914(−5)	2.144 792(−5)
9	2.991 860(−6)	8.567 874(−6)	6.937 594(−6)	6.954 706(−6)	6.948 156(−6)	6.951 880(−6)	6.733 312(−6)
10	9.874 776(−7)	2.843 079(−6)	2.305 277(−6)	2.313 382(−6)	2.311 603(−6)	2.317 913(−6)	2.260 000(−6)
11	4.382 822(−7)	1.364 300(−6)	1.118 129(−6)	1.122 613(−6)	1.121 929(−6)	1.121 845(−6)	1.098 459(−6)
				Shift Δ_s			
1	1.862 419(−3)	−4.174 002(−3)	−1.158 628(−3)	−1.175 177(−3)	−1.175 794(−3)	−1.173 611(−3)	−1.183 584 25(−3)
2	3.580 939(−4)	−3.512 037(−4)	5.620 598(−6)	9.038 625(−7)	2.388 532(−7)	5.480 105(−7)	−2.625 400 81(−6)
3	9.652 531(−5)	9.681 158(−5)	−1.906 334(−5)	−1.441 365(−5)	−1.377 065(−5)	−1.373 478(−5)	−2.150 642 92(−5)
4	1.932 362(−4)	−2.080 654(−4)	−5.499 020(−4)	−5.329 823(−4)	−5.300 642(−4)	−5.365 925(−4)	−5.652 220 72(−4)
5	2.372 199(−3)	−1.568 332(−4)	−1.397 789(−4)	−1.323 562(−4)	−1.317 235(−4)	−1.247 982(−4)	−1.121 665 74(−4)
6	6.269 459(−5)	−2.007 228(−4)	−1.636 043(−4)	−1.606 383(−4)	−1.600 431(−4)	−1.601 996(−4)	−1.510 775 97(−4)
7	2.965 730(−5)	−7.386 815(−5)	−4.058 619(−5)	−4.053 338(−5)	−4.047 335(−5)	−4.048 776(−5)	−3.880 319 47(−5)
8	1.297 110(−5)	−2.758 825(−5)	−1.199 159(−5)	−1.209 170(−5)	−1.208 980(−5)	−1.208 851(−5)	−1.171 531 14(−5)
9	5.115 783(−6)	−8.367 629(−6)	−3.133 724(−6)	−3.182 278(−6)	−3.184 647(−6)	−3.187 457(−6)	−3.111 425 91(−6)
10	2.174 737(−6)	−2.692 248(−6)	−9.167 560(−7)	−9.369 256(−7)	−9.383 768(−7)	−9.410 868(−7)	−9.222 313 65(−7)
11	1.314 824(−6)	−1.275 004(−6)	−4.025 160(−7)	−4.131 213(−7)	−4.140 280(−7)	−4.141 474(−7)	−4.067 447 13(−7)

The $^1S^e$ ground states of Li$^+$ and Ne^{8+} (i.e., the target wave functions), which are necessary to construct the corresponding $\mathcal{P}$ operator, are computed by including up to $N_2 = 40$ configurations as those defined in Eq. (19). The powers j_1 and j_2 ($j_1 \leqslant j_2$) range from 0 to 3, the angular momenta ℓ_i from 0 to 3, and the exponents α and β, which are common to all configurations and have been optimized for the full expansion, take the values $\alpha_i = 5.004\,54$ and $\beta_i = 3.265\,46$ for Li$^+$, and $\alpha_i = 16.681\,81$ and $\beta_i = 10.884\,86$ for Ne^{7+}. The calculated energies for the $^1S^e$ ground state of Li$^+$ and Ne^{8+} are, respectively, $-7.278\,311$ a.u. (to be compared with the experimental value $-7.279\,84$ a.u.) and $-93.904\,44$ a.u. (experimental value $-94.005\,53$ a.u.).

To calculate the resonant wave functions in $\mathcal{Q}$ subspace, we diagonalize the effective Hamiltonian of Eq. (16), with $M = 80$–100 a.u., in a large basis of configurations as those given in Eq. (17). $^2S^e$ resonances are obtained with $N_3 = 9740$ configurations built from STOs (2946 sss, 2600 pps, 1800 ppd, 1404 dds, and 972 ffs) for Li and with $N_3 = 7996$ configurations (2268 sss, 2093 pps, 1008 dds, 972 ppd, 810 pdf, 700 ffs, and 145 ddd) for Ne^{7+}. $^2P^o$ resonances are obtained with $N_3 = 10\,470$ configurations built from STOs (2700 ssp, 2520 ppp, 1056 spd, 1764 pdd, 1458 ppf, and 972 ffp) for Li and with $N_3 = 7000$ configurations (2700 ssp, 3240 ppp, 1056 spd, and 4 pdd) for Ne^{7+}. $^2D^e$ resonances are obtained with $N_3 = 9912$ configurations (2592 ssd, 1764 spp,

1764 ppd, 1296 sdd, 1344 spf, 576 sff, and 576 ffd) for Li and with $N_3 = 7000$ configurations (1800 ssd, 1470 spp, 1764 ppd, 1080 sdd, and 342 spf) for Ne^{7+}. The powers j_1, j_2, and j_3 ($j_1 \leqslant j_2 \leqslant j_3$) range from 0 to 5, the angular momenta ℓ_i from 0 to 3, and the exponents α_i, β_i, and γ_i are the terms of the *even-tempered* sequences $\alpha_i = \alpha_0/(n\eta^i)$, $\beta_i = \beta_0/(n\eta^i)$, and $\gamma_i = \gamma_0/(n\eta^i)$, where n is the principal quantum number ($n = 1$ for s functions, $n = 2$ for p functions and so on) and $\eta = 1.6$–2.0. The first term of these sequences is $\alpha_0 = \beta_0 = \gamma_0 = 20.0$ for Li. The basis for Ne^{7+} is the same as for Li but scaled by the factor 10/3. We have checked that slightly smaller basis sets lead to very similar results.

The $\mathcal{P}$ states are obtained by diagonalizing Eq. (7) in a basis of configurations as those defined in Eq. (20). In these configurations, the target wave function is in turn the CI expansion described earlier, and the third electron is described by s STOs for states of $^2S^e$ symmetry, p STOs for the $^2P^o$ symmetry, and d STOs for the $^2D^e$ symmetry. The exponents γ_k of the latter STOs are given by an *even-tempered* sequence containing $N_1 = 60$ STOs (120 STOs for $^2S^e$ symmetry). This leads to 60 (120) $\mathcal{P}$ states among which approximately half of them belong to the three-electron continuum. Some of the latter lie between the first and the second ionization thresholds, which is the region we are interested in. A complete calculation (for the largest basis sets) in each angular symmetry requires no more than 10 hours of CPU time in a desktop computer with 4GB of RAM memory and a single 2.2-GHz processor.

In Tables I and II we report the calculated energies $\mathcal{E}_s$, energy shifts Δ_s, and Auger widths Γ_s (corrected positions are given by $\mathcal{E}_s + \Delta_s$) for Li $^2S^e$, $^2P^o$, and $^2D^e$ resonances. All resonances lie close to the Li$^+$ ($1s2s$ ^3S) threshold, so even with the largest basis set used in this work, we only find a reduced number of them, namely, 11 resonances for the $^2S^e$ symmetry, 8 for the $^2P^o$ one, and 5 for the $^2D^e$ one. We have carefully investigated convergence of the calculated energies and widths with (i) the number of configurations used to diagonalize $\mathcal{Q}H\mathcal{Q}$, (ii) the number of $\mathcal{Q}$ states included in the optical potential $V_{\text{opt}}^{n\neq s}$ to build the $\mathcal{P}H'\mathcal{P}$ projected Hamiltonian, and (iii) the number of configurations used in the description of the target state to build the $\mathcal{P}$ projection operator. Concerning (i), we have reached good convergence for $N_3 \sim 10\,000$ configurations; beyond this number, linear dependencies begin to appear due to the limited (double) precision used in our computations. Concerning (ii), we have systematically increased the number of terms in the optical potential from 10 to 40 and we have found effective convergence for ~ 30 terms. The convergence with the number of configurations included in the target state [item (iii)] requires a more careful analysis. We have systematically increased this number from 1 up to 40 (for $N_2 > 40$, the first 6–7 significant figures are the same). The results obtained for 10, 20, 30, and 40 configurations are given in Table I. It can be seen that the widths and energy shifts obtained with a low number of terms in the target state are significantly far away from the converged result, especially for the most correlated symmetry, $^2S^e$. Previous theoretical calculations have only used one configuration to represent the target states [34,46]. As can be seen, the energies $\mathcal{E}_s + \Delta_s$ obtained with 1 and 40 configurations are relatively similar, but this is due to a

TABLE II. Energies, widths, and energy shifts for the lowest eight $^2P^o$ and five $^2D^e$ resonances of Li below the Li$^+$ $1s2s$ ^3S threshold located at $\sim -5.110\,86$ a.u.. The different columns show results obtained with the quasiprojector, $\mathcal{P}^0$, the full projector, $\mathcal{P}^0 + \Delta\mathcal{P}$, and the latter projector plus the polarization potential $V_{\text{opt}}^{n\neq s}$. Numbers between parentheses mean powers of 10; that is, $x(a) = x \times 10^a$.

	$\mathcal{P}^0$	$+\Delta\mathcal{P}$	$+\Delta\mathcal{P}$ & V_{opt}
$^2P^o$			
	Energy $\mathcal{E}_s$		
1	−5.312 551	−5.312 551	−5.312 551
2	−5.256 283	−5.256 280	−5.256 280
3	−5.183 306	−5.183 306	−5.183 306
4	−5.149 023	−5.149 024	−5.149 024
5	−5.133 396	−5.133 396	−5.133 396
6	−5.124 584	−5.124 584	−5.124 584
7	−5.121 588	−5.121 589	−5.121 589
8	−5.112 039	−5.112 039	−5.112 039
	Width Γ_s		
1	1.383 031(−4)	1.382 346(−4)	1.355 093(−4)
2	3.433 205(−4)	3.438 379(−4)	3.458 710(−4)
3	6.781 350(−6)	6.762 450(−6)	6.657 223(−6)
4	1.286 440(−6)	1.269 274(−6)	1.267 614(−6)
5	1.495 400(−6)	1.465 742(−6)	1.455 920(−6)
6	1.291 420(−5)	1.291 405(−5)	1.237 354(−5)
7	1.207 306(−5)	1.211 024(−5)	1.218 747(−5)
8	2.277 558(−5)	2.282 480(−5)	2.237 714(−5)
	Shift Δ_s		
1	7.250 953(−4)	7.250 392(−4)	7.233 526(−4)
2	4.312 365(−5)	4.304 486(−5)	4.392 076(−5)
3	2.071 525(−5)	2.071 395(−5)	2.085 019(−5)
4	7.436 367(−6)	7.434 603(−6)	7.451 878(−6)
5	3.191 842(−6)	3.188 896(−6)	3.191 990(−6)
6	3.990 832(−5)	3.990 920(−5)	3.921 396(−5)
7	4.633 286(−5)	4.633 767(−5)	4.657 914(−5)
8	6.462 687(−5)	6.459 138(−5)	6.454 336(−5)
$^2D^e$			
	Energy $\mathcal{E}_s$		
1	−5.232 980	−5.232 981	−5.232 981
2	−5.165 744	−5.165 744	−5.165 744
3	−5.141 545	−5.141 545	−5.141 545
4	−5.127 958	−5.127 958	−5.127 958
5	−5.111 720	−5.111 725	−5.111 725
	Width Γ_s		
1	3.841 651(−4)	3.841 523(−4)	3.826 705(−4)
2	3.571 943(−5)	3.571 782(−5)	3.570 541(−5)
3	1.074 925(−5)	1.074 862(−5)	1.073 578(−5)
4	8.638 463(−6)	8.639 843(−6)	8.627 641(−6)
5	4.818 978(−6)	4.810 805(−6)	4.800 652(−6)
	Shift Δ_s		
1	1.358 360(−4)	1.358 364(−4)	1.361 600(−4)
2	1.514 508(−5)	1.514 508(−5)	1.515 201(−5)
3	5.288 937(−6)	5.288 984(−6)	5.291 895(−6)
4	5.218 586(−6)	5.218 851(−6)	5.220 761(−6)
5	9.905 546(−6)	9.896 882(−6)	9.879 882(−6)

TABLE III. Comparison of parameters (positions and widths) for the lowest $^2S^e$ Li resonance states obtained with our approach, other theoretical calculations, and experimental data. Our values are reported relative to the nonrelativistic variational energy of the Li $1s^22s$ $^2S^e$ ground state ($-7.478\,060\,323\,650$ a.u.) from Yan *et al.* [48]. Energy values are given in eV and widths are reported in meV by using the conversion factor 1 a.u. $= 27.211\,383\,86M/(M + m_e) = 27.209\,233$ eV. Numbers between parentheses mean experimental uncertainty.

E_s (eV)				Γ_s (meV)		
This work						
$\mathcal{E}_s$	$\mathcal{E}_s + \Delta_s$	Other works	Experiment	This work	Other works	Experiment
$^2S^e$						
56.5503	56.5181	56.384[a]	56.395(15)[c]	69.61	37.34[a]	50(30)[f]
		58.389[b]	56.352(10)[f]		36.76[b]	
					40.3[e]	
62.0024	62.0024	61.989[a]	62.00(1.5)[c]	10.88	7.94[a]	
		61.991[b]	61.991(6)[d]		7.750[b]	
			61.995(10)[f]		13[e]	
63.1618	63.1612	63.145[a]	63.16(1.5)[c]	0.606	2.56[a]	
		62.144[b]	63.135(6)[d]		2.045[b]	
			63.17(3)[f]			
63.3927	63.3773	63.326[a]	63.311(6)[d]	2.959	0.16[a]	
		63.322[b]	63.35(3)[f]		0.402[b]	
63.5903	63.5872	63.573[a]	63.57(15)[c]	5.594	3.03[a]	
		63.571[b]	63.565(6)[d]		3.021[b]	
			63.58(3)[f]			
63.7423	63.7382	63.718[a]	63.735(6)[d]	4.149	1.46[a]	
		63.720[b]			1.630[b]	
63.9735	63.9725	63.951[a]	63.933(6)[d]	1.540	0.72[a]	
		63.951[b]			0.730[b]	
64.1259	64.1256			0.584		

[a]Verbockhaven and Hansen [46], CI truncated diagonalization method with relativistic corrections.
[b]Chung [47], saddle-point CI method with relativistic corrections.
[c]Rassi *et al.* [49], ejected electron spectroscopy, detection of electrons.
[d]McIlrath and Lucatorto [50], VUV absorption spectrum from $1s^22p$ $^2P^o$, detection of photons.
[e]Bhatia [11], CI calculation.
[f]Ziem *et al.* [51], collision experiment, detection of electrons.

compensation of errors. Indeed, Table I shows that, as the size of the target expansion is increased, the unshifted energies $\mathcal{E}_s$ increase, but the energy shifts decrease going in some cases from positive to negative values. Variation of the Auger widths with the number of terms included in the target expansion is even more pronounced: Converged values may be twice as large as those obtained by using a single configuration. Thus, a proper description of the target state included in the $\mathcal{P}$ projection operator is of utmost importance to obtain correct widths, especially for the most correlated states of Li: $^2S^e$.

We analyze now the effect of $\Delta\mathcal{P}$ (the second term in the $\mathcal{P}$ projection operator) and the optical potential $V_{\text{opt}}^{n\neq s}$ [see Eq. (5)]. Table I shows that, except for the first resonance, corrections to the energy due to $\Delta\mathcal{P}$ are very small and only affect the seventh significant figure; at variance, corrections to the widths and the energy shifts generally affect the third and the second significant figure, respectively. The optical potential affects at most the fifth significant figure of the energies and the second or the third of the widths, while energy shifts are much more sensitive (although they remain very small).

Table II shows our results for the $^2P^o$ and $^2D^e$ resonances. As can be seen, the effect of including $\Delta\mathcal{P}$ and the optical potential $V_{\text{opt}}^{n\neq s}$ is much less pronounced than for the $^2S^e$ resonances. This is the consequence of the fact that electrons in the $^2P^o$

and $^2D^e$ states, with dominant $1s^2np$ or $1s^2nd$ configurations, are much less correlated than in the $^2S^e$ ones, with dominant $1s^2ns$ configurations. In addition, the magnitude of the correction introduced by $\Delta\mathcal{P}$ in the $^2P^o$ and $^2D^e$ symmetries is significantly smaller than for the $^2S^e$ one. Indeed, the $\Delta\mathcal{P}$ correction depends very much on the value of λ_α eigenvalues [see Eq. (14)]. The λ_α eigenvalues resulting from the integral equation (15) are 1.003 33, 7.24109×10^2, 2.46063×10^4, 3.18371×10^4, 1.40807×10^8, etc., for the v_α functions with $\ell = 0$, 1.73055×10^3, 4.90117×10^4, 1.56482×10^6, 6.25689×10^7, 6.52206×10^7, etc., for those with $\ell = 1$, 5.93243×10^4, 6.77209×10^5, 1.28675×10^7, 2.64885×10^8, 1.88057×10^9, etc., for those with $\ell = 2$, and so on. Therefore, the most important corrections are expected for the states of $^2S^e$ symmetry, since the dominant configurations in the three-electron continuum state are of the form $(nsn's)v_\lambda(n''s)$. For the states of $^2P^e$ symmetry, the dominant configurations are of the form $(n\ell n'\ell)v_\lambda(n''p)$, but they contribute less due to the larger value of the λ_α eigenvalues.

We compare now our calculations with those of Verbockhaven and Hansen [46] who have reported the most comprehensive and complete study of resonance parameters for Li. These authors used a truncated diagonalization method (TDM), in which bound $1s^2n\ell$ and continuum $1s^2\epsilon\ell$

TABLE IV. Comparison of parameters (positions and widths) for the lowest eight $^2P^o$ and five $^2D^e$ resonance states in Li obtained with our approach, other theoretical calculations, and experimental data. Our values are reported relative to the nonrelativistic variational energy of the Li $1s^22s$ $^2S^e$ ground state ($-7.478\,060\,323\,650$ a.u.) from Yan *et al.* [48]. Energy values are given in eV and widths are reported in meV by using the conversion factor 1 a.u. $= 27.211\,383\,86 M/(M + m_e) = 27.209\,233$ eV. Numbers between parentheses mean experimental uncertainty.

E_s (eV)				Γ_s (meV)		
This work		Other works	Experiment	This work	Other works	Experiment
$\mathcal{E}_s$	$\mathcal{E}_s + \Delta_s$					
$^2P^o$						
58.9218	58.9415	58.908[a]	58.911(6)[d]	3.68	3.78[a]	2.6(1)[f]
		58.910[b]	58.912(15)[h]		3.33[b]	3.2(6)[g]
		58.929[c]				
60.4529	60.4541	60.407[a]	60.398(3)[d]	9.40	9.97[a]	
		60.398[b]	60.405(15)[h]		9.56[b]	
		60.420[c]				
62.4385	62.4390	62.421[a]	62.420(3)[d]	0.182	0.20[a]	
		62.417[b]	62.422(10)[e]		0.203[b]	
		62.424[c]	62.421(15)[h]			
63.3713	63.3715	63.356[a]	63.357(9)[d]	0.0348	0.04[a]	
		63.351[b]	63.353(10)[e]		0.0445[b]	
		62.356[c]	63.35(1.5)[h]			
63.7965	63.7966	63.753[a]	63.755(3)[d]	0.0397	0.05[a]	
		63.750[b]	63.752(10)[e]		0.0445[b]	
		63.755[c]	63.755(15)[h]			
64.0363	64.0373	63.953[a]	63.952(3)[d]	0.334	0.15[a]	
		63.950[b]	63.951(10)[e]		0.140[b]	
		63.962[c]	63.955(15)[h]			
64.1178	64.1190	64.062[a]	64.048(9)[d]	0.328	0.50[a]	
		64.050[b]	64.050(10)[e]		0.391[b]	
			64.045(15)[h]			
64.3776	64.3793			0.602		
$^2D^e$						
61.0869	61.0906	61.062[a]	61.060(6)[k]	10.4	11.01[a]	10.5(3)[f]
		61.099[i]	61.065(15)[h]		10.72[i]	
		61.060[j]			10.63[j]	
62.9164	62.9168	62.901[a]	62.897(6)[k]	0.972	0.99[a]	0.89(4)[f]
		62.933[i]	62.93(1.5)[h]		1.03[i]	
		63.903[j]			0.997[j]	
63.5748	63.5750	63.560[a]	63.565(6)[k]	0.292	0.30[a]	
		63.578[i]	63.57(1.5)[h]		12.48[i]	
		63.562[j]			0.313[j]	
63.9445	63.9446	63.867[a]	63.865(6)[k]	0.235	0.14[a]	
		63.869[j]			0.132[j]	
64.3862	64.3864	64.042[a]		0.131	0.08[a]	
		64.037[j]			0.0638[j]	

[a]Verbockhaven and Hansen [46], CI truncated diagonalization method with relativistic corrections.
[b]Chung [47], saddle-point CI method with relativistic corrections.
[c]Jaskòlska and Woźnicki [52], saddle-point correlated CI method, here recalculated with the ground-state energy from Yan *et al.* [48].
[d]Ederer *et al.* [53], absorption spectroscopy from the ground state, detection of photons.
[e]Kiernan *et al.* [54], synchrotron radiation, photoion detection.
[f]Cederquist and Mannervik [55], beam foil spectroscopy, detection of photons
[g]Pedrotti [56], extinction spectroscopy.
[h]Rassi *et al.* [49], ejected electron spectroscopy, detection of electrons.
[i]Brage *et al.* [57], nonrelativistic MCHF.
[j]Chung [58], saddle-point CI method with relativistic corrections.
[k]McIlrath and Lucatorto [50], VUV absorption spectrum from $1s^22p$ $^2P^o$, detection of photons.

configurations associated with the lowest ionic limit $1s^2$ $^1S^e$ in Li$^+$ are removed from the Hamiltonian matrix before diagonalization. In other words, in the TDM, one avoids constructing three-electron CI configurations that include two $1s$ orbitals. The number of configurations used in Ref. [46] to diagonalize $\mathcal{Q}H\mathcal{Q}$ is larger than ours, 20 000 configurations compared to our $\sim$10 000. This is because they construct CI wave functions in terms of B-spline basis sets, which do not exhibit the problem of linear dependencies when the basis set is increased. However, they used a simple Hartree-Fock (HF) approximation to represent the two-electron target state and the $\mathcal{P}$ projection operator (i.e., a single configuration), while in our method we use a fully correlated two-electron $^1S^e$ state for Li$^+$. This serious limitation was recognized by Verbockhaven and Hansen [46], who suggested that their reported widths might be affected by an error of 10%. Another difference with the calculations reported in Ref. [46] is that we did not include relativistic corrections (however, the magnitude of these corrections was not reported in [46]).

In Tables III and IV we compare our results for Li with those of Ref. [46] and other representative theoretical results (we refer to [46] for a full list of references). A noticeable aspect in Table III for the $^2S^e$ states is the discrepancy between our reported widths and those obtained by other authors [46,47]. The only available experimental value for the width of the lowest $^2S^e$ resonance is 50 meV; ours is $\sim$70 meV and other theories report a value of $\sim$37 meV. Interestingly, the widths of the seven lowest $^2S^e$ states that are obtained by only including one configuration in the Li$^+$ target state (first column of Table I) are 33, 6.8, 2.0, 0.15, 2.9, 1.3, and 0.62 meV, which are in good agreement with the values reported in previous theoretical works. This suggests that the errors of the widths reported in [46,47] are mostly due to the use of a quasiprojector instead of the full projector $\mathcal{P} = \mathcal{P}^0 + \Delta\mathcal{P}$. To settle this question, more precise experiments and additional theoretical calculations are required.

In the case of the $^2P^o$ and $^2D^e$ resonances (see Table IV), our calculated energy positions are slightly above those obtained with other theories and the experimental values. In this respect, it is worth noticing that our reported energies in eV are given relative to the best nonrelativistic value available for the Li ground state [48] using correlated STOs. A meaningful comparison with existing theoretical values should be made on absolute scale, but, unfortunately, absolute energies have not been reported in previous works. In contrast, our widths for the $^2P^o$ and $^2D^e$ resonances compare fairly well with those obtained by other authors and with experiment.

Tables V, VI, and VII present our calculated energies $\mathcal{E}_s$, energy shifts Δ_s, and Auger widths Γ_s (resonance positions are given by $\mathcal{E}_s + \Delta_s$) for Ne^{7+} resonances: 12 for the $^2S^e$ symmetry, 12 for the $^2P^o$ symmetry, and 13 for the $^2D^e$ symmetry. At variance with Li, the convergence for Ne^{7+} is much faster and 7000 configurations ($\sim$8000 for $^2S^e$) in the $\mathcal{Q}$ subspace turn out to be enough to produce converged parameters for at least the first five or six resonances. As expected, the effect of $\Delta\mathcal{P}$ and the optical potential $V_{opt}^{n\neq s}$ is even smaller than for Li, in particular for the lowest $^2S^e$ resonance whose width is fairly well approximated by neglecting $\Delta\mathcal{P}$.

TABLE V. Energies, widths and energy shifts for the lowest $^2S^e$ resonances of Ne^{7+}, below the Ne^{8+} $1s2s$ ^3S threshold located at $\sim$−60.7446 a.u.. The different columns show results obtained with the quasiprojector, $\mathcal{P}^0$, the full projector, $\mathcal{P}^0 + \Delta\mathcal{P}$, and the latter projector plus the polarization potential $V_{opt}^{n\neq s}$. Numbers between parentheses mean powers of 10; that is, $x(a) = x \times 10^a$.

	$\mathcal{P}^0$	$+\Delta\mathcal{P}$	$+\Delta\mathcal{P}$ & V_{opt}
$^2S^e$			
		Energy $\mathcal{E}_s$	
1	−69.924 705	−69.910 649	−69.910 649
2	−68.467 983	−68.461 159	−68.461 159
3	−64.493 814	−64.490 151	−64.490 151
4	−64.237 966	−64.235 483	−64.235 483
5	−63.866 757	−63.865 956	−63.865 956
6	−63.674 726	−63.673 218	−63.673 218
7	−62.722 492	−62.719 988	−62.719 988
8	−62.419 103	−62.417 849	−62.417 849
9	−62.314 878	−62.314 354	−62.314 354
10	−62.090 691	−62.090 463	−62.090 463
11	−61.892 305	−61.889 907	−61.889 907
12	−61.602 050	−61.601 778	−61.601 778
		Width Γ_s	
1	4.894 609(−3)	4.252 310(−3)	4.269 312(−3)
2	1.019 109(−3)	1.128 854(−3)	1.121 754(−3)
3	1.469 632(−3)	1.297 279(−3)	1.297 878(−3)
4	8.153 126(−4)	7.408 758(−4)	7.428 670(−4)
5	9.691 857(−5)	1.090 318(−4)	1.088 390(−4)
6	1.108 557(−4)	1.351 661(−4)	1.328 509(−4)
7	6.043 355(−4)	5.509 588(−4)	5.507 438(−4)
8	3.009 324(−4)	2.706 820(−4)	2.710 401(−4)
9	2.412 345(−5)	3.175 870(−5)	3.113 609(−5)
10	4.359 345(−7)	1.692 879(−6)	1.692 457(−6)
11	3.326 019(−4)	3.086 182(−4)	3.083 624(−4)
12	6.322 974(−5)	5.689 576(−5)	5.670 167(−5)
		Shift Δ_s	
1	3.699 802(−4)	−3.501 276(−4)	−3.652 470(−4)
2	−4.755 620(−3)	−4.966 355(−3)	−4.963 349(−3)
3	4.766 093(−5)	−1.054 702(−4)	−1.042 928(−4)
4	2.339 218(−4)	1.237 723(−4)	1.208 976(−4)
5	−4.054 414(−4)	−4.642 386(−4)	−4.668 882(−4)
6	−9.463 546(−4)	−1.000 716(−3)	−9.959 118(−4)
7	−1.056 247(−4)	−1.608 655(−4)	−1.605 708(−4)
8	8.760 870(−5)	4.398 725(−5)	4.335 870(−5)
9	−2.929 645(−4)	−3.251 548(−4)	−3.244 643(−4)
10	−8.000 863(−5)	−1.013 552(−4)	−1.010 787(−4)
11	−1.199 550(−4)	−1.495 869(−4)	−1.491 098(−4)
12	1.321 742(−6)	−1.028 244(−5)	−1.089 415(−5)

The number of theoretical works on autoionizing states of Ne^{7+} is very scarce. To our knowledge, there are only three works available [60–62] based on the use of the saddle-point method. Kramida and Ivanov [63] have compiled experimental data for Ne^{7+} and performed some computations using Vainshtein's MZ codes [64] and Cowan's programs [65] to interpret the assignment of observed transition lines. In

TABLE VI. Energies, widths and energy shifts for the lowest 12 $^2P^o$ resonances of Ne^{7+}, below the Ne^{8+} $1s2s$ ^3S threshold located at ~ -60.7446 a.u.. The different columns show results obtained with the quasiprojector, $\mathcal{P}^0$, the full projector, $\mathcal{P}^0 + \Delta\mathcal{P}$, and the latter projector plus the polarization potential $V_{opt}^{n \neq s}$. Numbers between parentheses mean powers of 10; that is, $x(a) = x \times 10^a$.

	$\mathcal{P}^0$	$+\Delta\mathcal{P}$	$+\Delta\mathcal{P}$ & V_{opt}
$^2P^o$			
		Energy $\mathcal{E}_s$	
1	−69.333 41	−69.333 26	−69.333 26
2	−69.114 18	−69.114 17	−69.114 17
3	−64.445 69	−64.445 67	−64.445 67
4	−64.121 08	−64.120 92	−64.120 92
5	−64.030 50	−64.030 18	−64.030 18
6	−63.901 96	−63.901 84	−63.901 84
7	−63.796 26	−63.796 23	−63.796 23
8	−63.565 72	−63.565 70	−63.565 70
9	−62.724 56	−62.724 55	−62.724 55
10	−62.396 33	−62.395 46	−62.395 46
11	−62.353 65	−62.353 24	−62.353 24
12	−62.275 73	−62.275 72	−62.275 72
		Width Γ_s	
1	1.691 274(−4)	1.690 092(−4)	1.643 188(−4)
2	2.128 602(−3)	2.128 571(−3)	2.132 957(−3)
3	3.157 598(−5)	3.161 926(−5)	3.173 868(−5)
4	5.316 022(−7)	4.584 772(−7)	6.251 708(−7)
5	8.040 476(−4)	8.065 038(−4)	8.079 433(−4)
6	1.689 050(−4)	1.673 312(−4)	1.658 195(−4)
7	4.459 518(−6)	4.395 444(−6)	4.342 631(−6)
8	2.430 830(−6)	2.457 976(−6)	2.441 934(−6)
9	3.658 605(−5)	3.656 545(−5)	3.658 070(−5)
10	5.409 124(−5)	5.147 872(−5)	5.157 439(−5)
11	2.992 349(−4)	3.044 220(−4)	3.045 857(−4)
12	4.497 584(−7)	4.873 757(−7)	4.787 996(−7)
		Shift Δ_s	
1	2.413 462(−3)	2.413 451(−3)	2.411 143(−3)
2	8.934 335(−5)	8.889 332(−5)	9.080 107(−5)
3	7.778 932(−5)	7.779 942(−5)	7.767 047(−5)
4	1.870 044(−4)	1.884 983(−4)	1.870 056(−4)
5	5.976 183(−4)	5.952 459(−4)	5.962 961(−4)
6	6.521 083(−5)	6.622 074(−5)	6.664 819(−5)
7	1.489 796(−5)	1.508 387(−5)	1.514 836(−5)
8	3.211 098(−4)	3.209 863(−4)	3.211 344(−4)
9	2.911 952(−5)	2.915 550(−5)	2.916 125(−5)
10	−3.588 942(−6)	−3.540 663(−6)	−3.488 289(−6)
11	2.506 461(−4)	2.499 749(−4)	2.498 536(−4)
12	2.001 742(−6)	1.967 549(−6)	1.973 520(−6)

TABLE VII. Energies, widths, and energy shifts for the lowest 12 $^2D^e$ resonances of Ne^{7+}, below the Ne^{8+} $1s2s$ ^3S threshold located at ~ -60.7446 a.u.. The different columns show results obtained with the quasiprojector, $\mathcal{P}^0$, the full projector, $\mathcal{P}^0 + \Delta\mathcal{P}$, and the latter projector plus the polarization potential $V_{opt}^{n \neq s}$. Numbers between parentheses mean powers of 10; that is, $x(a) = x \times 10^a$.

	$\mathcal{P}^0$	$+\Delta\mathcal{P}$	$+\Delta\mathcal{P}$ & V_{opt}
$^2D^e$			
		Energy $\mathcal{E}_s$	
1	−68.891 89	−68.891 89	−68.891 89
2	−64.260 78	−64.260 78	−64.260 78
3	−63.954 02	−63.954 02	−63.954 02
4	−63.920 31	−63.920 30	−63.920 30
5	−63.729 06	−63.729 06	−63.729 06
6	−62.675 42	−62.675 42	−62.675 42
7	−62.310 63	−62.310 63	−62.310 63
8	−62.302 42	−62.302 41	−62.302 41
9	−62.172 39	−62.172 39	−62.172 39
10	−62.068 82	−62.068 82	−62.068 82
11	−61.940 86	−61.940 85	−61.940 85
12	−61.559 67	−61.559 66	−61.559 66
		Width Γ_s	
1	3.194 127(−3)	3.194 142(−3)	3.192 746(−3)
2	1.123 234(−4)	1.123 333(−4)	1.119 912(−4)
3	2.804 081(−5)	2.804 081(−5)	2.743 577(−5)
4	4.149 861(−4)	4.149 813(−4)	4.144 623(−4)
5	8.747 417(−4)	8.747 355(−4)	8.758 858(−4)
6	2.394 918(−5)	2.395 017(−5)	2.393 616(−5)
7	3.325 807(−4)	3.325 761(−4)	3.320 086(−4)
8	7.332 321(−6)	7.329 808(−6)	7.866 038(−6)
9	1.901 330(−9)	1.899 660(−9)	2.094 176(−9)
10	2.429 795(−4)	2.429 773(−4)	2.430 964(−4)
11	4.984 582(−6)	4.984 551(−6)	4.999 672(−6)
12	1.840 667(−4)	1.842 297(−4)	1.841 458(−4)
		Shift Δ_s	
1	1.122 062(−3)	1.122 080(−3)	1.122 414(−3)
2	7.326 813(−5)	7.326 550(−5)	7.329 864(−5)
3	1.037 055(−4)	1.037 058(−4)	1.036 631(−4)
4	1.442 213(−4)	1.442 228(−4)	1.446 739(−4)
5	1.985 504(−4)	1.985 531(−4)	1.982 598(−4)
6	1.895 758(−5)	1.895 943(−5)	1.895 916(−5)
7	1.217 880(−4)	1.217 872(−4)	1.217 630(−4)
8	3.216 047(−5)	3.216 818(−5)	3.224 025(−5)
9	6.999 764(−6)	6.999 801(−6)	7.000 429(−6)
10	4.987 502(−5)	4.987 596(−5)	4.982 772(−5)
11	8.637 081(−6)	8.640 592(−6)	8.636 653(−6)
12	8.292 269(−5)	8.294 523(−5)	8.305 816(−5)

Table VIII we compare our data in eV with other available theoretical results and with experimental results from NIST compiled by Kramida and Ivanov [63]. It can be seen that our results compare fairly well with the existing data. We have also included in Table VIII the predictions obtained by the saddle-point method [61,62] when relativistic corrections are taken into account. We could not find in the literature a better value for the ground-state energy of Ne^{8+} (with relativistic corrections) than the one calculated by Chung [59] and this value was used with the resonance energies

given in Refs. [61,62] to compose the relativistic values quoted in Table VIII. These relativistic positions clearly overestimate the experimental values, but the reason remains unclear to us, unless a better correct value for the ground state is available. However, nonrelativistic values seem to provide good precisions for positions and widths to compare with experimental data. We cannot judge the quality of the theoretical results given in Ref. [63] since there are no specific details on the computational procedure and a further analysis would be only a guess.

TABLE VIII. Comparison of the lowest $^2S^e$, $^2P^o$, and $^2D^e$ Ne^{7+} resonance parameters obtained with our approach, other theoretical calculations, and experimental values. Our values are reported relative to the nonrelativistic variational energy for the Ne^{7+} $1s^2 2s$ $^2S^e$ ground state ($-102.682\,231\,482\,398$ a.u.) from Yan *et al.* [48]. For relativistic values of energy positions denoted with (r) we make use of the relativistic ground-state energy ($-102.804\,800\,322$ a.u.) given by Chung [59]. Energy values are given in eV and widths are reported in meV by using the conversion factor 1 a.u. $= 27.211\,383\,86M/(M + m_e) = 27.210\,644$ eV. Experimental values are taken from NIST [66] as compiled by Kramida and Ivanov [63].

| E_s (eV) | | | | Γ_s (meV) | | |
| This work | | Other works | Experiment | This work | Other works | Experiment |
$\mathcal{E}_s$	$\mathcal{E}_s + \Delta_s$					
$^2S^e$						
891.736	891.726	891.078[c]	891.5207	116.2	81.1[c]	
931.177	931.042	930.778[c]	932.1875	30.52	11.3[c]	
1039.231	1039.228		1039.112	35.32		
1046.161	1046.164		1045.063	20.21		
1056.216	1056.203		1057.337	2.962		
1061.460	1061.433			3.615		
1087.398	1087.394			14.99		
1095.620	1095.621			7.375		
1098.436	1098.427			0.847		
1104.528	1104.526			0.0461		
1109.985	1109.981			8.391		
$^2P^o$						
907.447	907.513	907.376[a] 907.295; 908.292(r)[b] 907.273; 908.243(r)[c] 908.023[d]	907.899	4.47	6.12[a] 4.0[b] 3.9[c]	
913.409	913.411	913.148; 914.164(r)[b] 913.147; 914.134(r)[c] 913.946[d]	913.912	58.0	52.94[a] 51.3[b] 53.5[c]	
1040.44	1040.44	1040.648[d]	1041.59	0.864		
1049.28	1049.28	1049.906[d]	1050.15	0.0170		
1051.74	1051.76	1051.163[d]	1052.13	21.9		
1055.24	1055.24			4.51		
1058.11	1058.11		1057.09	0.118		
1064.39	1064.39			0.0664		
1087.27	1087.27			0.995		
1096.23	1096.23			1.40		
1097.38	1097.38			8.29		
1099.49	1099.49			0.0130		
$^2D^e$						
919.457	919.487	919.324;920.568(r)[b] 919.323;920.530(r)[c] 920.451[d]	920.384	86.9	77.8[b] 77.5[c]	
1045.47	1045.47	1045.77[d]	1046.01	3.06		
1053.82	1053.82		1054.11	0.763		
1054.74	1054.74	1054.87[d]	1054.86	11.3		
1059.94	1059.95	1059.76[d]	1060.07	23.8		
1088.61	1088.61	1089.15[d]	1089.08	0.652		
1098.54	1098.54			9.03		
1098.76	1098.76			0.200		
1102.30	1102.30			5.17×10^{-5}		
1105.12	1105.12			6.61		
1108.60	1108.60			0.136		
1118.97	1118.97			5.01		
1119.09	1119.09			0.355		

[a]Wu and Xi [60], nonrelativistic saddle-point with R-matrix method.
[b]Gou and Deng [61], saddle-point with complex rotation method (nonrelativistic and with relativistic corrections).
[c]Zhu *et al.* [62], saddle-point with complex rotation method (nonrelativistic and with relativistic corrections).
[d]Kramida and Ivanov [63], compilation and fitting of experimental data, and theoretical predictions using MZ and Cowan's codes.

IV. CONCLUSION

We have presented a method for computing resonant states of three-electron atomic systems, which is based on the Feshbach projection formalism and includes ingredients that are usually neglected in implementations of this formalism: (i) the term that guarantees idempotency of the projection operators, (ii) the nonresonant optical potential and (iii) a proper converged description of the target state. The method has been used to compute energy positions and autoionization widths of the lowest $^2S^e$, $^2P^o$, and $^2D^e$ autoionizing states of Li and Ne^{7+}, for which electron correlation is expected to play a quite different role. We have shown that inclusion of these extra terms play a minor role in the evaluation of the resonant positions. In contrast, for the $^2S^e$ states of Li, the neglect of (iii) can lead to errors in the autoionization widths as large as 100%. A similar conclusion was anticipated in 1986 by Berk *et al.* [33] for the $^2S^e$ resonances of He$^-$, but the limited capacity of the computer resources available in those days prevented these authors from performing an accurate evaluation of the different terms. At variance with Li, our results for Ne^{7+} show that the contribution of the extra terms (i) and (ii) is almost irrelevant. Implementation of the present approach with other basis sets, such as *B* splines, and inclusion of relativistic corrections is in progress.

[1] M. Drescher *et al.*, Nature (London) **419**, 803 (2002).
[2] R. Kienberger *et al.*, Nature (London) **427**, 817 (2004).
[3] M. Wickenhauser, J. Burgdörfer, F. Krausz, and M. Drescher, Phys. Rev. Lett. **94**, 023002 (2005).
[4] M. S. Schöffler *et al.*, Science **320**, 920 (2008).
[5] H. Feshbach, Ann. Phys. (NY) **19**, 287 (1962).
[6] A. Temkin and A. K. Bhatia, in *Autoionization: Recent Developments and Applications*, edited by A. Temkin (Plenum Press, New York, 1985), p. 1.
[7] I. Sánchez and F. Martín, Phys. Rev. A **44**, 7318 (1991).
[8] A. Temkin, A. K. Bhatia, and J. N. Bardsley, Phys. Rev. A **5**, 1663 (1972).
[9] A. K. Bhatia and A. Temkin, Phys. Rev. A **13**, 2322 (1976).
[10] A. Temkin and A. K. Bhatia, Phys. Rev. A **18**, 792 (1978).
[11] A. K. Bhatia, Phys. Rev. A **18**, 2523 (1978).
[12] S. Wakid, A. K. Bhatia, and A. Temkin, Phys. Rev. A **21**, 496 (1980).
[13] A. K. Bhatia and A. Temkin, Phys. Rev. A **23**, 3361 (1981).
[14] M. Bylicki, Phys. Rev. A **40**, 1748 (1989).
[15] L. Rosenberg, Phys. Rev. A **53**, 4151 (1996).
[16] M. Bylicki, Phys. Rev. A **41**, 2386 (1990).
[17] K. T. Chung, Phys. Rev. A **20**, 1743 (1979).
[18] K. T. Chung and B. F. Davis, in *Autoionization: Recent Developments and Applications*, edited by A. Temkin (Plenum Press, New York, 1985), p. 73.
[19] M. Bylicki, Phys. Rev. A **39**, 3316 (1989).
[20] K. T. Chung, Phys. Rev. A **41**, 4090 (1990).
[21] M. Bylicki, Phys. Rev. A **41**, 4093 (1990).
[22] C. A. Nicolaides, Phys. Rev. A **46**, 690 (1992).
[23] W. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).
[24] B. Junker, Adv. At. Mol. Phys. **18**, 208 (1982).
[25] N. Moiseyev, Phys. Rep. **302**, 212 (1998).
[26] J. L. Sanz-Vicario and E. Lindroth, Phys. Rev. A **65**, 060703(R) (2002); J. L. Sanz-Vicario, E. Lindroth, and N. Brandefelt, *ibid.* **66**, 052713 (2002).
[27] J. L. Sanz-Vicario and E. Lindroth, Phys. Rev. A **68**, 012702 (2003).
[28] J. L. Sanz-Vicario, J. C. Cardona, and E. Lindroth, Phys. Rev. A **78**, 053411 (2008).
[29] P. Lambropoulos, P. Maragakis, and J. Zhang, Phys. Rep. **305**, 203 (1998).
[30] M. A. Lysaght, H. W. van der Hart, and P. G. Burke, Phys. Rev. A **79**, 053411 (2009).
[31] J. L. Sanz-Vicario, H. Bachau, and F. Martín, Phys. Rev. A **73**, 033410 (2006).
[32] A. Temkin and A. K. Bhatia, Phys. Rev. A **31**, 1259 (1985).
[33] A. Berk, A. K. Bhatia, B. R. Junker, and A. Temkin, Phys. Rev. A **34**, 4591 (1986).
[34] P. Galan, Ph.D. thesis, Université de Bordeaux I, 1990.
[35] F. Martín, O. Mó, A. Riera, and M. Yáñez, Europhys. Lett. **4**, 799 (1987).
[36] F. Martín, O. Mó, A. Riera, and M. Yáñez, J. Chem. Phys. **87**, 6635 (1987).
[37] A. Macías, F. Martín, A. Riera, and M. Yáñez, J. Chem. Phys. **91**, 376 (1989).
[38] J. C. Cardona and J. L. Sanz-Vicario, J. Phys. B **41**, 055003 (2008).
[39] J. C. Cardona, Ph.D. thesis, Universidad de Antioquia, Medellín, Colombia, 2008.
[40] Z.-C. Yan and G. W. F. Drake, J. Phys. B **30**, 4723 (1997).
[41] S. Larsson, Phys. Rev. **169**, 49 (1968).
[42] I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer, Berlin, 1982).
[43] R. J. Tweed, J. Phys. B **5**, 810 (1972).
[44] A. Macías, F. Martín, A. Riera, and M. Yáñez, Int. J. Quantum Chem. **33**, 279 (1988).
[45] A. Macías, F. Martín, A. Riera, and M. Yáñez, Phys. Rev. A **36**, 4179 (1987).
[46] G. Verbockhaven and J. E. Hansen, J. Phys. B **34**, 2337 (2001).
[47] K. T. Chung, Phys. Rev. A **56**, R3330 (1997).
[48] Z.-C. Yan, M. Tambasco, and G. W. F. Drake, Phys. Rev. A **57**, 1652 (1998).
[49] D. Rassi, V. Pejcev, and K. J. Ross, J. Phys. B **10**, 3535 (1977).
[50] T. J. McIlrath and T. B. Lucatorto, Phys. Rev. Lett. **38**, 1390 (1977).
[51] P. Ziem, R. Bruch, and N. Stolterfoht, J. Phys. B **8**, L480 (1975).
[52] B. Jaskòlska and W. Woźnicki, Phys. Scr. **39**, 230 (1989).

[53] D. L. Ederer, T. Lucatorto, and R. P. Madden, Phys. Rev. Lett. 25, 1537 (1970).

[54] L. M. Kiernan *et al.*, J. Phys. B **29**, L181 (1996).

[55] H. Cederquist and S. Mannervik, Phys. Rev. A **31**, 171 (1985).

[56] K. D. Pedrotti, Opt. Commun. **62**, 250 (1987).

[57] T. Brage, C. F. Fischer, and N. Vaeck, J. Phys. B **26**, 621 (1993).

[58] K. T. Chung, Phys. Rev. A **57**, 3518 (1998).

[59] K. T. Chung, Phys. Rev. A **44**, 5421 (1991).

[60] L. Wu and J. Xi, J. Phys. B **24**, 3351 (1991).

[61] B. Gou and W. Deng, Phys. Rev. A **62**, 032705 (2000).

[62] J. J. Zhu, B. C. Gou, and Y. D. Wang, J. Phys. B **41**, 065702 (2008).

[63] A. E. Kramida and I. A. Ivanov, Phys. Scr. **56**, 264 (1997).

[64] L. A. Vainshtein and U. I. Safronova, At. Data Nucl. Data Tables **25**, 311 (1980).

[65] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).

[66] National Institute of Standards and Technology (NIST), Atomic Spectra DataBase [http://physics.nist.gov/].