

Theory of the resonances of the LoSurdo-Stark effect

Cleanthes A. Nicolaidis and Spyros I. Themelis

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece

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When an atom or a molecule is exposed to an electric field, the discrete electronic spectrum turns into a spectrum of resonances with complex energies due to the mixing of the bound wave function of each unperturbed stationary state with the asymptotic form of the Airy function. The complex energies are eigenvalues of a non-Hermitian Schrödinger equation whose solutions have a special outgoing-wave asymptotic form, which is derived rigorously. At least three coordinate transformations (rotation, translation, and a combination of these) regularize the dc-field-induced resonance function, the most efficient one being the long-honored rotation, $f(x) = xe^{i\theta}$, which causes the function to dissipate asymptotically as $e^{-\gamma x^{3/2}}$. This finding, obtained from first principles, explains previous results that have been obtained either via trial computations or via elaborate mathematical analyses of the spectrum. The theory is further developed toward the efficient computation of such resonances with \mathcal{L}^2 functions. Starting from the resonance-wave-function form $\Psi^{\text{res}} = a\Psi_0 + bX_{\text{as}}$, the computation of the localized Ψ_0 is carried out on the real axis, and only the free-electron function belonging to X_{as} is rotated and optimized in the complex plane. Two applications are presented. The first involves a numerically solvable one-dimensional model of a shape resonance in a dc field for a large range of field strengths. The second involves the hydrogen atom in its ground as well as in its first excited state. In the first example, Ψ_0 is obtained numerically in an explicitly constructed effective potential containing partly the effect of the field. To this “dressed” Ψ_0 , the asymptotic part X_{as} is then added as a sum of an only ten back-rotated complex Slater-type orbitals (STO’s), whose coefficients and nonlinear parameter are optimized from the diagonalization of the full Hamiltonian until stability of the complex eigenvalue is achieved. In the second example, Ψ_0 was chosen as the exact $1s$ for the ground state and as the two roots $2s \pm 2p_0$ of the total Hamiltonian for the excited state. X_{as} was expressed in terms of angular momentum symmetry blocks up to $l = 8$, with each symmetry expanded in terms of ten complex STO’s. No optimization of θ or other nonlinear parameters was done. Comparison with the exact results for the model potential and with published ones for the H atom shows very good agreement, thereby demonstrating the efficiency and reliability of the theory as well as its potential for treating N -electron systems.

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I. INTRODUCTION

The phenomenon of the broadening and shifting of the energy of an atomic state when perturbed by an external dc field—the LoSurdo-Stark effect [1,2]—has led over the years to a variety of theoretical investigations as regards the resulting spectrum and its computation [2–20].

The mixing of the initially bound stationary states with the electronic continuum through the dc-field interaction, $V(z) = -eFz$, gives rise to nonstationary states (resonances) with complex energies (see below). In the 1970s, a series of publications initiated the interest in the use of complex scaling in the Hamiltonian coordinates, $\rho = re^{i\theta}$, for the computation of resonances using square-integrable basis sets [21–26,5,6]. The mathematical prerequisite for the rigorous application of this approach was that the potential $V(\mathbf{x})$ is “dilationally analytic,” a property which follows only if $V(\mathbf{x}) \xrightarrow{x \rightarrow \infty} 0$. Thus the unbounded linear potential $-eFz$, giving rise to the dc-field-induced resonances of the LoSurdo-Stark effect, is not included in the original theory of the spectrum of rotated Hamiltonians. Yet, computational experimentation

by Reinhardt [5] (see also Ref. [6]), following the method of Doolen [25], showed that converged results were obtained when the complex-scaled hydrogen atom plus dc-field Hamiltonian was diagonalized and the complex energy was stabilized as a function of θ or of the number of basis functions. Reinhardt [5] and Cerjan *et al.* [6] commented on this fact and emphasized the need for an explanation of the numerical results.

Given this situation, a series of rather esoteric mathematical analyses was published [9–12] which justified *a posteriori* the validity of the complex-coordinate-rotation (CCR) method. In the meantime, the coordinate translation, $x \rightarrow x + iq$, was also found to yield the resonances created by the linear potential [6–8]. In fact, Cerjan *et al.* [6] applied both methods to a model one-dimensional potential (their Eq. 4.1) and found that with the same basis the convergence of the coordinate rotation method was better.

Although the mathematical papers [7–12] seem to offer a justification for the effect of coordinate rotation and translation on the spectrum of the atom-plus-field Hamiltonian, it is desirable to have an alternative theory of LoSurdo-Stark resonances, written in the language of

the physicist, which offers a simple yet rigorous explanation of the relevance of the aforementioned coordinate transformations while allowing for the development of efficient computational methods. The purpose of this paper is to present such a theory and to demonstrate it by applying it to a model problem of a shape resonance in a dc field [27] as well as to the hydrogen atom in its ground and first excited states. It is shown how the complex-eigenvalue resonance spectrum is created and how these coordinate transformations emerge as a necessity for the regularization of the resonance wave function, thereby allowing the definition and solution of the problem in the space of two sets of state-specific \mathcal{L}^2 functions, optimized separately on the real coordinate axis and in the complex plane.

II. DERIVATION OF THE COMPLEX-EIGENVALUE SCHRÖDINGER EQUATION FOR THE LoSURDO-STARK RESONANCES

The problem of the LoSurdo-Stark resonance states can be treated in terms of a theory whose foundations involve the concepts of dynamic localization (represented by the square-integrable wave function Ψ_0), of the perturbation of the asymptotic boundary conditions (yielding effective Hermitian or non-Hermitian operators, depending on the function space), and of the exact form of the resonance function specific to the problem of interest [Ref. (28), Eqs. (1)–(14) and related discussion, and Refs. [29–34]].

The turning on of the external dc field transforms each stationary and localized atomic or molecular state Ψ_0 of real energy E_0 into a nonstationary one, which decays by emitting an electron. In the energy-dependent picture, the exact scattering function in the vicinity of an isolated decaying state (resonance) is a mixture of a bound component Ψ_0 with unbound ones, $U(r;E)$, which is written as [35]

$$\Psi(r;E) = a(E)\Psi_0 + \int dE' b_{E'}(E)U(r;E') \quad (1a)$$

$$= a(E) \left[\Psi_0 + P \int dE' \frac{V_{0E'}}{E-E'} U(r;E') + \lambda(E)V_{0E}U(r;E) \right] \quad (1b)$$

where

$$H_0\Psi_0 = E_0\Psi_0, \quad H_0 = H - V, \quad (2a)$$

$$V_{0E} = \langle U(r;E) | H | \Psi_0 \rangle, \quad (2b)$$

$$E = E_0 + P \int dE' \frac{|V_{0E'}|^2}{E-E'} + \lambda(E)|V_{0E}|^2. \quad (3)$$

Equation (3) constitutes the definition of the function $\lambda(E)$ whose value is fixed by the asymptotic boundary conditions of the problem [36].

Equation (1) contains all the information on and off resonance. $\Psi(E)$, being a scattering state, satisfies

$$(H - E)\Psi(r;E) = 0 \quad (4)$$

where E is a real number on the positive energy axis and not an eigenvalue.

Is there a time-independent *eigenvalue* equation that is satisfied on resonance? In order to answer this question we must impose the boundary conditions which a decaying state must satisfy. Thus we start from Eq. (1b) and seek to determine its asymptotic form pertaining to each nonstationary situation under study. To achieve this, we must know the corresponding asymptotic expression for the basis functions $U(r;E)$. Nicolaides, Komninos, and Mercouris [31] and Komninos and Nicolaides [32] have already done this in the case of atomic resonances for a short-range potential (negative ions) as well as for the long-range Coulomb potential. As is well known, the short-range potential was considered by Siegert [37] in his S -matrix treatment of nuclear resonances and led to the outgoing boundary conditions with complex momenta, previously introduced *ad hoc* by Gamow [38].

The Siegert-type treatment is rather alien to the problem of showing the emergence of the resonance spectrum of the LoSurdo-Stark effect. On the contrary, the present physically motivated theory is general, requiring only the appropriate restructuring of Eq. (1) by incorporating explicitly the asymptotic form of the $U(r;E)$ for each Ψ_0 representing a localized state of the unperturbed spectrum.

In the case of the LoSurdo-Stark problem, the atom-plus-field potential in the asymptotic region is dominated by

$$V(x) = -Fx. \quad (5)$$

The well-known energy-normalized asymptotic solution corresponding to $V(x)$ of Eq. (5) is the asymptotic form of the Airy function

$$U(k) \underset{\xi \rightarrow \infty}{\sim} \left[\frac{2}{\pi k} \right]^{1/2} \sin \left[\frac{k^3}{3F} + \frac{\pi}{4} + \delta \right]. \quad (6)$$

The term $k^3/3F + \pi/4$ is the usual JWKB phase [20] $\int^x dx' \sqrt{2(E + Fx')} + \pi/4$, with the JWKB local momentum $k(x)$ given by

$$k^2 = 2(E + Fx) - (2F)^{2/3}\xi, \quad F \text{ is real}, \quad (7)$$

$$\xi = \left[x + \frac{E}{F} \right] (2F)^{1/3}, \quad F \text{ is the field strength}. \quad (8)$$

Let

$$L \equiv \frac{k^3}{3F} + \frac{\pi}{4} + \delta. \quad (9)$$

Substituting Eq. (6) in (1b) we obtained

$$\psi(x) \underset{x \rightarrow \infty}{\sim} -\pi Va \left[\frac{2}{\pi k} \right]^{1/2} \left[\frac{1}{2} \left[1 - \frac{\lambda(E)}{i\pi} \right] e^{iL} + \frac{1}{2} \left[1 + \frac{\lambda(E)}{i\pi} \right] e^{-iL} \right]. \quad (10)$$

On resonance, the coefficient of the incoming wave must be zero, so that

$$\lambda(E) = -i\pi \text{ on resonance.} \quad (11)$$

Therefore on resonance the energy of Eq. (4) becomes complex,

$$E \rightarrow z_0 = E_0 + P \int dE' \frac{|V_{0E'}|^2}{E - E'} - i\pi |V_{0E}|^2 \quad (12a)$$

$$= E_0 + \Delta - \frac{i}{2} \Gamma. \quad (12b)$$

In lowest order, $\Delta \approx \Delta(E_0)$ and $\Gamma \approx \Gamma(E_0)$. In general, the extent of energy dependence of Δ and Γ depends on the characteristics of the nonstationary state, on the strength of the effective perturbation, and on the functions used in actual computations to represent the localized and the asymptotic components [30].

According to Eq. (7), the momentum also becomes complex

$$k^2 = 2(z_0 + Fx) \text{ on resonance.} \quad (7')$$

Given Eqs. (10)–(12), the exact asymptotic form of the resonance function for the dc-field-induced nonstationary state is

$$\Psi_{\text{res}}(k) \underset{\xi \rightarrow \infty}{\sim} -\pi V a \left(\frac{2}{\pi k} \right)^{1/2} \exp \left[i \left(\frac{k^3}{3F} + \frac{\pi}{4} + \delta \right) \right]. \quad (13)$$

V and a are evaluated at E_0 or in its neighborhood.

Thus it follows from the above development that by imposing the correct boundary conditions, Eq. (4) is transformed into a *complex-eigenvalue Schrödinger equation* (CESE)

$$(H - z_0)\Psi^{\text{res}} = 0 \quad (14)$$

[whose asymptotic solution $\Psi_{\text{as}}^{\text{res}}$ is given by Eq. (13)] which is satisfied by the eigenfunctions of nonstationary states created by the presence of the dc field corresponding to each Ψ_0 . In other words, for any atom or molecule the electronic discrete spectrum turns into a resonance spectrum [39]. The solution Ψ^{res} is not square integrable and its explicit asymptotic form is given by Eq. (13).

III. COORDINATE TRANSFORMATIONS EMERGING FROM THE REGULARIZATION OF Ψ^{res}

The solution of the CESE, Eq. (14), is facilitated if the norm problem is circumvented. This is possible if an appropriate coordinate transformation is found which effects a perturbation of boundary conditions in the asymptotic region such that the CESE of Eq. (14) can turn into an equivalent CESE whose solution is square integrable, with real or complex functions, while the Hamiltonian becomes non-Hermitian with the same complex eigenvalue. In other words, we should search for a transformation, $f(x)$, such that the differential equation is satisfied for two nearly equal boundary conditions, B_0 and B ,

$$B_0(f(x)) = B(x) \quad (15)$$

[Eq. (5.22) of Ref. [30]] where B_0 is the asymptotic un-

perturbed boundary condition, Eq. (13), and B is the perturbed one, defined operationally by restricting the function space to that of square-integrable functions. This changes the form of the Hamiltonian. Considered in Hilbert space, the difference between the old and the new forms constitutes the perturbation that causes the decay (Ref. [30], pp. 481–483).

The choice $f(r) = \rho = re^{i\theta}$ for the regularization of resonances of short-range potentials—also valid for the Coulomb potential—was introduced by Dykhne and Chaplik [40]. In the present case, the potential in the asymptotic region does not die out but instead it grows linearly with x [Eq. (5)]. Let us then consider the exponential form of Eq. (13) which determines the convergence properties of the LoSurdo-Stark resonance

$$\Psi^{\text{res}}(x, z_0) \underset{r \rightarrow \infty}{\sim} e^{i\alpha(z_0 + Fx)^{3/2}} \quad (16)$$

where α is a real constant. It is shown in the Appendix that the transformations

$$f_1(x) = x + iq, \quad q > \frac{\Gamma}{2F} \quad (17a)$$

$$f_2(x) = xe^{i\theta}, \quad 0 < \theta < \frac{2\pi}{3} \quad (17b)$$

$$f_3(x) = xe^{i\theta} - \frac{z_0}{F}, \quad 0 < \theta < \frac{2\pi}{3} \quad (17c)$$

make Ψ^{res} square integrable.

Thus, given the equivalence between transformed Hamiltonians with \mathcal{L}^2 bases and untransformed Hamiltonians with complex functions (e.g., Refs. [24] and [30], Secs. 5 and 7), these results explain the previous numerical and mathematical findings [5–12] in a simple and physically meaningful way and, of course, they are applicable to any one-electron or N -electron atomic state.

Furthermore, for the first time a formal understanding as to the computational characteristics of these two transformations emerges: By comparing Eqs. (A12) and (A18), which show the rate of exponential convergence to zero for transformations $f_1(x)$ and $f_2(x)$ correspondingly, we see that the complex rotation converges faster. This is in agreement with the numerical findings of Cerjan *et al.* [6] on their model potential (see their Table VI). Since this is a general result, we conclude that the complex rotation [Eq. (17b)] is indeed a computationally convenient transformation with good convergence properties for the dc- as well as the ac-field problem (in the Floquet framework). This fact is in accordance with the numerical results demonstrating the reasonably efficient representation of the outgoing orbitals in terms of back-rotated Slater-type orbitals in the many-electron, many-photon theory (MEMPT) of ac-field-induced energy widths and shifts [41–43].

IV. THEORY FOR THE SOLUTION OF THE CESE

The theory of the previous sections allows the undertaking of well-defined computational steps in order to treat realistic problems in conjunction with efficient methods for computing the relevant function spaces.

The very derivation of the CESE, Eq. (14), shows that the resonance N -particle wave function should have the form

$$\Psi = a\Psi_0 + bX_{as} \quad (18)$$

where

$$X_{as} = A[X_{core}(r_1, \dots, r_{N-1}) \otimes g_N(r_N)], \quad (19)$$

A is the antisymmetrizer, X_{core} represents the bound part of the ionized system, and $g_N(r_N)$ is the unbound orbital with

$$g_N(0) = 0, \quad g_N(r_N) \underset{r \rightarrow \infty}{\sim} \text{outgoing wave [Eq.(13)]}. \quad (20)$$

For reasons given above, we consider the rotation transformation. Equation (16) becomes

$$\Psi(\rho) = a(\theta)\Psi_0(\rho) + b(\theta)X_{as}(\rho), \quad |a|^2 + |b|^2 = 1. \quad (21)$$

This form is a basic feature of the present theory, making possible the efficient solution of Eq. (14) for a variety of resonance problems [29–32,41–45]. The choice and computation of Ψ_0 depends on the state under consideration and is in accordance with the notion of dynamic localization and of the boundary conditions of square integrability on the real axis.

The corresponding non-Hermitian energy matrix, $\mathbf{E}(\theta)$, contains the matrix elements $\langle \Psi_0(\rho), H(\rho), \Psi_0(\rho) \rangle$, $\langle \Psi_0(\rho), H(\rho), X_{as}(\rho) \rangle$, $\langle X_{as}(\rho), H(\rho), X_{as}(\rho) \rangle$. Application of mathematical analysis applicable to integrals of analytic functions [29] as well as explicit demonstration on solvable bound-state systems such as the hydrogen atom and the harmonic oscillator, and on the usual matrix elements with Slater-type orbitals (STO's) and Gaussian-type orbitals (GTO's), led to the conclusion [29–31] that for the bound function Ψ_0 the following invariance property holds:

$$\langle \Psi_0(\rho), H(\rho), \Psi_0(\rho) \rangle = \langle \Psi_0(r), H(r), \Psi_0(r) \rangle = E_0. \quad (22)$$

Equations (21) and (22) imply that the energy matrix $\mathbf{E}(\theta)$ can be written as

$$\mathbf{E}(\theta) = \begin{pmatrix} E_0 & \langle \Psi_0 | H | X_{as} \rangle \\ \langle X_{as} | H | X_{as} \rangle & \langle X_{as} | H | X_{as} \rangle \end{pmatrix} \quad (23)$$

whose size depends only on the size of the expansions of the unbound orbitals $g_N(\rho_N)$ for each channel, since both Ψ_0 and $X_{core}(N-1)$ and their expectation values are fixed from previous calculations on the real axis. The actual computation of the matrix elements $\langle \Psi_0(\rho), H(\rho), X_{as}(\rho) \rangle$ and $\langle X_{as}(\rho), H(\rho), X_{as}(\rho) \rangle$ can be carried out over complex coordinates or over real and complex coordinates, depending on the type of square-integrable basis sets used to expand the rotated orbital $g_N(\rho_N)$ [29–31,41–45]. A choice of $g_N(\rho_N)$ which is convenient for use with *numerical* (and therefore accurate) zeroth-order bound orbitals belonging to Ψ_0 or to $X_{core}(N-1)$ is to expand the square-integrable $g_N(\rho_N)$ for each channel i in terms of Sturmians, of STO's, or of

GTO's of real coordinates. Thus

$$g^i(\rho) \rightarrow \sum_n a_n \phi_n^i(r) \quad (24)$$

where the g^i are coupled to the symmetry adapted core $X_{core}(N-1)$ to form angular momentum states. When the back rotation [Eq. (22)] is applied to the two matrix elements, for the bound functions Ψ_0 and X_{core} as well as for the Hamiltonian, ρ is replaced by r while for the basis set of Eq. (24) r is replaced by $\rho^* = re^{-i\theta}$.

How is the optimization of the various g^i achieved when the basis set expansion, Eq. (24), is used and the φ_n are made functions of $\rho^* = re^{-i\theta}$? For this work, two criteria have been used. The first refers to the identification of the correct solution from the diagonalized complex matrix. The state-specific construction of Ψ and the accurate description of the localized wave function Ψ_0 are features which allow the search for that root which is closest to the pair (Ψ_0, E_0) with

$$\bar{z}_0 = E_0 + \bar{\Delta} - \frac{i}{2} \bar{\Gamma}, \quad (25)$$

$$\langle \bar{\Psi}, \Psi_0 \rangle \approx \max \text{ for all values of } F. \quad (26)$$

The second criterion concerns the stabilization of the complex eigenvalue as a function of nonlinear parameters $(\theta, a_1, a_2, \dots)$ or as a function of the size of the $\langle \phi_n \rangle$ set [24,25,41–45].

V. APPLICATION TO A MODEL OF A SHAPE RESONANCE IN A dc FIELD

The work from this institute on a variety of resonance states using complex scaling has aimed at the efficient solution of many-electron problems (e.g., [30,41–45,34], and references therein). However, given the general interest in model potentials for studying resonances (e.g., [24,6,18,33,46–55]), in this section we exhibit the implementation of the theory on a model of a shape resonance in a dc field. We had two reasons for choosing this model. The first is that it can be solved exactly by numerical integration and, therefore, provide a rigorous check for the more general expansion method. The second is that by choosing a shape resonance as the unperturbed state, the opportunity is given for underlining concepts of imposed boundary conditions in the choice of Ψ_0 and of the explicit construction of the related field-dressed effective Hamiltonian.

We have considered the exponential potential $V(x) = 7.5x^2e^{-x}$, first used by Bain *et al.* [24], which has been a favorite test case for application of theories of resonances (e.g., [24,33,47–50]). The full potential is

$$V(x; F) = 7.5x^2e^{-x} - Fx, \quad x \geq 0. \quad (27)$$

The physics implied by $V(x; F)$ is interesting in general, since one has to define a physically meaningful square-integrable Ψ_0 . For example, in the case of autoionizing or predissociating resonances, criteria for choosing Ψ_0 include the state-specific self-consistent calculation, the satisfaction of the virial theorem (which is an index of localization) and the existence of the correct number of

nodes in the zeroth-order function [28,30,34]. For many-electron atoms and diatomics, these are made possible by the computation of a numerical multi-configuration Hartree-Fock (MCHF) zeroth-order function [28,30,34,44].

In the present case of the local potential, the appropriate choice of Ψ_0 is achieved by introducing an effective potential, $V_0(x;F)$,

$$V_0(x;F) = \begin{cases} V(x;F), & x \leq x_0 \\ V(x_0;F), & x > x_0 \end{cases} \quad (28)$$

where x_0 is the value of x for which $V(x;F)$ acquires its maximum value [56].

The corresponding Ψ_0 is computed via numerical integration on the real axis. The resulting "dressed" localized function depends intrinsically on the external field strength F and constitutes a very good approximation to the resonance function.

As regards the description of the asymptotic part X_{as} , we used back-rotated Slater-type orbitals

$$\varphi_n(\rho^*) \sim \rho^{*n} e^{-\alpha\rho^*}. \quad (29)$$

These were not orthogonalized on Ψ_0 or among themselves so that the complex energy z_0 is found from the solution of the generalized non-Hermitian eigenvalue problem

$$\mathbf{HC} = z_0 \mathbf{SC} \quad (30)$$

on the function space $\{\Psi_0$ (numerical); φ_n (analytic) $\}$. The optimization of the calculation was carried out using the stability criteria

$$\left[\frac{\partial z}{\partial \theta} \right]_{z=z_0} = 0, \quad \left[\frac{\partial z}{\partial \alpha} \right]_{z=z_0} = 0 \quad (31)$$

while the number of STO's for all values of the field strength—from 0.00 to 1 a.u.—was kept small (ten) and constant. This was done in order to demonstrate the efficiency of the theory and the importance of separating Ψ and choosing a physically relevant Ψ_0 on the real axis [29,30]. In order to test the accuracy of this theoretical approach comparison was made with exact answers, obtained by numerically integrating in the complex plane

the Schrödinger equation for $H(\theta)$, $\theta=0.7$ rad.

The results are shown in Table I. The agreement between the variational results and the exact ones is very good for real and imaginary parts over the entire range of field strengths.

VI. APPLICATION TO THE GROUND AND THE FIRST EXCITED STATE OF THE HYDROGEN ATOM

The LoSurdo-Stark resonances of the hydrogen atom in its ground or excited states have been computed by a number of theories which obtain complex energies (e.g., see Refs. [2–6,12–20]). We have treated this problem in spherical coordinates (in which it is not separable), since this coordinate system is suitable for the treatment of N -electron atomic states. The perturbed Hamiltonian is

$$H = h + Fr \cos\alpha, \quad (32)$$

h is the free hydrogen Hamiltonian, and α is the angle between the field and the radius vector.

For the ground state, Ψ_0 was chosen as the exact $1s$ function. For the excited state, two Ψ_0 's were employed, the $2s \pm 2p_0$ as obtained from the diagonalization of the atom-field interaction. In this case, the field dependence of Ψ_0 is only through the mixing coefficients of the hydrogenic $2s$ and $2p_0$ functions and not through the radial function, as in the model problem of Sec. V. As regards the choice of X_{as} , we opted for a systematic increase of the number of angular momentum blocks until stability is reached. Thus, l blocks up to $l=8$ were used, each of which had a radial expansion of ten back-rotated complex STO's of the form $\rho^{*n+l} e^{-\alpha\rho^*}$, $n=0, \dots, 9$. The values of θ and of α were fixed at $\theta=0.4$ and $\alpha=1$. Their optimization would reduce the size of the overall expansion or the detailed accuracy of the calculation. However, given the demonstration of the theory and its good convergence (see below and Tables II and III), we did not spend time with the optimization of the nonlinear parameters or with different choices of back-rotated basis functions. It appears that this expansion spans the perturbed inner and outer regions of these resonances sufficiently well.

The results for a range of field strengths are presented

TABLE I. Real and imaginary parts (in a.u.) of the complex eigenvalue of the Hamiltonian with $V(x;F)$ given by Eq. (27), as a function of the field strength F (in a.u.). The exact results are obtained by numerical integration of the rotated Hamiltonian. The expansion-based results are obtained with a numerical Ψ_0 corresponding to $V_0(x;F)$ of Eq. (28) and an optimized set of ten ϕ_n [Eq. (24)]. The values of the nonlinear parameters (θ, α) are chosen according to the stability criteria [Eq. (31)].

F	α	θ	Re E	Im E	Re E (ex)	Im E (ex)
0.00	2.10	0.149	3.4266	0.0127	3.4264	0.0128
0.01	2.12	0.149	3.4168	0.0136	3.4165	0.0134
0.02	2.20	0.150	3.4069	0.0150	3.4066	0.0150
0.05	2.16	0.150	3.3772	0.0165	3.3768	0.0163
0.10	1.99	0.150	3.3255	0.0200	3.3267	0.0203
0.20	1.58	0.150	3.2252	0.0308	3.2257	0.0302
0.50	2.23	0.150	2.9132	0.0746	2.9174	0.0751
1.00	1.75	0.185	2.3997	0.2004	2.4020	0.1974

in Tables II and III for the ground state and for the two excited states, respectively. There are many published results on the complex eigenvalues of the H atom in a dc field, especially for the ground state. Most of them have been cited here and in the papers by Silverman and Nicolaides [19]. The accuracy of some of them is extremely high, as concluded from the large number of significant digits [2,12,19]. However, in the present work such accuracy was deemed unnecessary. Rather, we wanted to see whether reasonable accuracies can be obtained for a range of field strengths with only small and even unoptimized expansions.

Thus, for the sake of comparison, we chose two sets from two different theories. For the ground state, we compare (Table II) with the results of Ref. [19], obtained from a variationally implemented large-order perturbation theory coupled with analytic continuation techniques to account for the complex eigenvalue (see also Refs. [15] and [2]). For the two excited states, we compare with the pioneering results of Cerjan *et al.* [6] obtained with the CCR method (see also Ref. [12] for results with additional significant digits and Ref. [19] for results on high- n states). Both comparisons exhibit good agreement.

VII. CONCLUSION

The theory of this paper shows how the resonances of the LoSurdo-Stark effect emerge as states of a CESE with special asymptotic boundary conditions, [Eq. (14)], how their wave functions can be regularized, and how they can be computed efficiently and accurately in terms of separately optimized \mathcal{L}^2 functions representing Ψ_0 and X_{as} [Eq. (18)].

As regards applications, of special importance is the state-specific calculation of the localized Ψ_0 , which constitutes the part of the resonance function defined on the real coordinate axis. In the present calculations on the H atom, spherical coordinates were employed and Ψ_0 was chosen as the hydrogenic function for the 1s state and as the dc-field diagonalized ($2s \pm 2p_0$) functions for the first excited state. These prototype calculations show how the theory can be applied for the systematic and economic treatment of N -electron states in dc fields. For example,

such applications have already been made on the ground state of negative ions [41–43].

Furthermore, we have considered the case where part of the effect of the field is incorporated in the radial characteristics of Ψ_0 . In the case of nonstationary states of the field-free Hamiltonian, such as autoionizing or predissociating, the strength of the interactions is fixed and Ψ_0 is computed once from an internally consistent eigenvalue equation for the effective Hamiltonian QHQ , where the projection operator $Q = |\Psi_0\rangle\langle\Psi_0|$ [28,30,34]. In the case of field-induced resonances, the interaction is field-strength dependent. Therefore an optimal representation of Ψ_0 in principle ought to take this fact into account, especially when the state of interest is affected by a strong field. In the present model study of Sec. V, this is achieved by computing an intrinsically field-dependent Ψ_0 by first identifying QHQ with $V_0(x, F)$, the effective potential of Eq. (28). The use of “field-dressed” Ψ_0 will probably prove necessary for the many-electron, many-photon treatment of atoms and molecules in intense ac fields (see Sec. I of Ref. [57]).

APPENDIX

We wish to find transformations $f(x)$ which render the unnormalizable function [Eq. (16)] a square-integrable one. Let

$$w = |w|e^{i\phi} = z_0 + Fx = E - \frac{i}{2}\Gamma + Fx \quad (\text{A1a})$$

where

$$|w| = \left[(E + Fx)^2 + \left(\frac{\Gamma}{2} \right)^2 \right]^{1/2}, \quad (\text{A1b})$$

$$\phi = \tan^{-1} \left[-\frac{\Gamma}{2(E + Fx)} \right]. \quad (\text{A1c})$$

Then

$$\Psi^{\text{res}}(x, z_0) \underset{x \rightarrow \infty}{\sim} \exp \left[i\alpha |w|^{3/2} \cos \frac{3\varphi}{2} \right] \times \exp \left[-\alpha |w|^{3/2} \sin \frac{3\varphi}{2} \right]. \quad (\text{A2})$$

TABLE II. Complex eigenvalues for the ground state of hydrogen in a dc field (in a.u.). See text.

F (a.u.)	This work		Ref. [19]	
	$-E$	$-i\Gamma/2$	$-E$	$-i\Gamma/2$
0.04	0.503 772	0.194×10^{-5}	0.503 772	0.194×10^{-5}
0.07	0.513 077	$0.923\ 58 \times 10^{-3}$	0.513 077	$0.923\ 68 \times 10^{-3}$
0.10	0.527 419	$0.726\ 83 \times 10^{-2}$	0.527 418	$0.726\ 90 \times 10^{-2}$
0.15	0.551 067	$0.300\ 20 \times 10^{-1}$	0.551 031	$0.300\ 19 \times 10^{-1}$
0.20	0.570 145	$0.606\ 00 \times 10^{-1}$	0.570 181	$0.606\ 15 \times 10^{-1}$
0.25	0.585 028	$0.947\ 89 \times 10^{-1}$	0.585 270	$0.948\ 24 \times 10^{-1}$
0.30	0.596 701	0.130 59	0.596 723	0.130 67
0.40	0.613 369	0.204 69	0.613 141	0.204 75
0.50	0.623 068	0.280 22	0.623 068	0.279 74
0.70	0.631 312	0.428 45	0.630 712	0.428 83
1.00	0.626 772	0.653 32	0.624 337	0.646 82

TABLE III. (a) Complex eigenvalues for the first excited state, $2s + 2p_0$, in a dc field (in a.u.). See text. (b) Complex eigenvalues for the first excited state, $2s - 2p_0$, in a dc field (in a.u.). See text.

(a)					
F (a.u.)	This work			Ref. [6]	
	$-E_0^a$	$-E$	$-i\Gamma/2$	$-E$	$-i\Gamma/2$
0.005	0.139 981	0.142 624	0.5262×10^{-4}	0.142 62	0.5297×10^{-4}
0.010	0.154 917	0.166 088	0.5448×10^{-2}	0.166 09	0.5442×10^{-2}
0.015	0.169 811	0.187 636	0.1688×10^{-1}	0.187 62	0.1689×10^{-1}
0.020	0.184 649	0.206 667	0.3041×10^{-1}	0.206 68	0.3039×10^{-1}
0.025	0.199 425	0.223 978	0.4480×10^{-1}	0.224 04	0.4483×10^{-1}
0.030	0.214 131	0.240 435	0.5984×10^{-1}	0.240 15	0.5983×10^{-1}
0.035	0.228 754	0.255 222	0.7525×10^{-1}	0.255 29	0.7522×10^{-1}

(b)					
F (a.u.)	This work			Ref. [6]	
	$-E_0^a$	$-E$	$-i/2\Gamma$	$-E$	$-i/2\Gamma$
0.005	0.109 982	0.112 063	0.2537×10^{-5}	0.120 62	0.2860×10^{-5}
0.010	0.094 931	0.103 888	0.1632×10^{-2}	0.103 89	0.1637×10^{-2}
0.015	0.079 851	0.096 899	0.7566×10^{-2}	0.096 945	0.7537×10^{-2}
0.020	0.064 744	0.088 966	0.1539×10^{-1}	0.088 941	0.1549×10^{-1}
0.025	0.049 614	0.080 177	0.2434×10^{-1}	0.080 011	0.2422×10^{-1}
0.030	0.034 462	0.069 980	0.3279×10^{-1}	0.070 490	0.3321×10^{-1}
0.035	0.019 291	0.060 240	0.4181×10^{-1}	0.060 629	0.4222×10^{-1}

^a 2×2 diagonalization of the Hamiltonian in the basis $2s, 2p_0$.

It is the second term which must be regularized. We have for $x \rightarrow \infty$

$$\sin \frac{3\phi}{2} \underset{x \rightarrow \infty}{\sim} -\frac{1}{x}. \quad (\text{A3})$$

Since $|w| \sim x$, it follows from (A2) and (A3) that $\Psi(x, z_0)$ diverges as

$$\Psi(x, z_0) \underset{x \rightarrow \infty}{\sim} e^{\delta x^{1/2}}, \quad \delta > 0. \quad (\text{A4})$$

Now consider a transformation $x \rightarrow f(x)$. Then,

$$w \rightarrow w' = |w'| e^{i\varphi'} = E - \frac{i}{2}\Gamma + Ff(x), \quad (\text{A5a})$$

$$\varphi' = \arg w' = \tan^{-1} \left[\frac{\text{Im} w'}{\text{Re} w'} \right], \quad (\text{A5b})$$

and Ψ^{res} becomes square integrable if

$$|w'|^{3/2} \sin \frac{3\varphi'}{2} \underset{x \rightarrow \infty}{\sim} \lambda x^\gamma, \quad \gamma > 0, \lambda > 0. \quad (\text{A6})$$

Let

$$f_1(x) = x + iq. \quad (\text{A7})$$

Then

$$w'_1 = E + Fx + i \left[Fq - \frac{\Gamma}{2} \right] \quad (\text{A8})$$

so that, as $x \rightarrow \infty$,

$$|w'_1| \underset{x \rightarrow \infty}{\sim} x, \quad \varphi'_1 = \tan^{-1} \left[\frac{Fq - \Gamma/2}{E + Fx} \right]. \quad (\text{A9})$$

The quantity $E + Fx$ is positive for $x \rightarrow \infty$. Thus, if

$$q > \frac{\Gamma}{2F}, \quad (\text{A10})$$

then $\varphi'_1 \sim 1/x$,

$$\sin \frac{3\varphi'_1}{2} \underset{x \rightarrow \infty}{\sim} \frac{\lambda_1}{x}. \quad (\text{A11})$$

Combining Eqs. (A7)–(A11) we see that indeed condition (A6) is satisfied:

$$|w'_1| \sin \frac{3\varphi'_1}{2} \underset{x \rightarrow \infty}{\sim} \lambda_1 x^{1/2}, \quad \lambda_1 > 0. \quad (\text{A12})$$

Now, let

$$f_2(x) = xe^{i\theta}. \quad (\text{A13})$$

Then,

$$w'_2 = |w'_2| e^{i\varphi'_2} = E + Fxe^{i\theta} - \frac{i}{2}\Gamma, \quad (\text{A14})$$

$$|w'_2| = [(E + Fx \cos\theta)^2 + (Fx \sin\theta - \Gamma/2)^2]^{1/2}, \quad (\text{A15a})$$

$$\varphi'_2 = \tan^{-1} \left[\frac{Fx \sin\theta - \Gamma/2}{E + Fx \cos\theta} \right]. \quad (\text{A15b})$$

As $x \rightarrow \infty$

$$|w'_2| \underset{x \rightarrow \infty}{\sim} x, \quad (\text{A16a})$$

$$\varphi'_2 \underset{x \rightarrow \infty}{\sim} \theta. \quad (\text{A16b})$$

Therefore $\Psi^{\text{res}}(f_2(x), z_0)$ is square integrable if

$$\sin \frac{3\varphi'_2}{2} = \sin \frac{3\theta}{2} > 0$$

or, if

$$0 < \theta < \frac{2\pi}{3} \quad (\text{A17})$$

in which case

$$|w'_2|^{3/2} \sin \frac{3\varphi'_2}{2} \sim \lambda_2 x^{3/2}, \quad \lambda_2 > 0. \quad (\text{A18})$$

Finally, the combination of rotation with translation

$$f_3(x) = x e^{i\theta} - \frac{z_0}{F} \quad (\text{A19})$$

is also a regularizing transformation.

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- [1] N. Ryde, *Atoms and Molecules in Electric Fields* (Almqvist & Wiksells, Stockholm, 1975).
- [2] H. J. Silverstone, in *Atoms in Strong Fields*, edited by C. A. Nicolaides, C. W. Clark, and M. H. Nayfeh (Plenum, New York, 1990), p. 295; V. Franceschini, V. Grecchi, and H. J. Silverstone, *Phys. Rev. A* **32**, 1338 (1985).
- [3] E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second-Order Differential Equations* (Oxford University, London, 1958), Vol. II.
- [4] M. Hehenberger, H. V. McIntosh, and E. Brändas, *Phys. Rev. A* **10**, 1494 (1974).
- [5] W. P. Reinhardt, *Int. J. Quantum Chem.* **S10**, 359 (1976).
- [6] C. Cerjan, R. Hedges, C. Holt, W. P. Reinhardt, K. Scheibner, and J. J. Wendoloski, *Int. J. Quantum Chem.* **14**, 393 (1978).
- [7] J. E. Avron and I. Herbst, *Commun. Math. Phys.* **52**, 239 (1977).
- [8] C. Cerjan, W. P. Reinhardt, and J. E. Avron, *J. Phys. B* **11**, L201 (1978).
- [9] I. W. Herbst and B. Simon, *Phys. Rev. Lett.* **41**, 67 (1978).
- [10] I. W. Herbst, *Commun. Math. Phys.* **64**, 279 (1979).
- [11] I. W. Herbst, and B. Simon, *Commun. Math. Phys.* **80**, 181 (1981).
- [12] S. Graffi and V. Grecchi, *Commun. Math. Phys.* **62**, 83 (1978); L. Benassi and V. Grecchi, *J. Phys. B* **13**, 911 (1980).
- [13] O. Atabek and R. Lefebvre, *Int. J. Quantum Chem.* **19**, 901 (1981).
- [14] A. Macias and A. Riera, *J. Phys. B* **14**, 955 (1981).
- [15] W. P. Reinhardt, *Int. J. Quantum Chem.* **21**, 3 (1982).
- [16] R. J. Damburg and V. Kolosov, in *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge University, Cambridge, England, 1983), p. 31.
- [17] T. P. Grozdanov, P. S. Krstic, M. J. Rakovic, and E. A. Solovev, *Phys. Lett. A* **132**, 262 (1988).
- [18] G. Alvarez and H. J. Silverstone, *Phys. Rev. A* **40**, 3690 (1989); *Phys. Rev. Lett.* **63**, 1364 (1989).
- [19] J. N. Silverman and C. A. Nicolaides, in *Atoms in Strong Fields*, edited by C. A. Nicolaides, C. W. Clark, and M. H. Nayfeh (Plenum, New York, 1990), p. 309; *Chem. Phys. Lett.* **153**, 61 (1988); *Chem. Phys. Lett.* **184**, 321 (1991).
- [20] D. A. Harmin, in *Atoms in Strong Fields*, edited by C. A. Nicolaides, C. W. Clark, and M. H. Nayfeh (Plenum, New York, 1990), p. 61.
- [21] J. Aquilar and J. M. Combes, *Commun. Math. Phys.* **52**, 239 (1971).
- [22] E. Balslev and J. M. Combes, *Commun. Math. Phys.* **22**, 280 (1971).
- [23] B. Simon, *Ann. Math.* **97**, 247 (1973).
- [24] R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukumar, *J. Phys. B* **7**, 2189 (1974).
- [25] G. Doolen, *J. Phys. B* **8**, 525 (1975).
- [26] For papers on the progress that had been made until early 1978, see the issue on complex scaling, *Int. J. Quantum Chem.* **14** (1978).
- [27] Such a physical situation was first computed by the CCR method by J. J. Wendoloski and W. P. Reinhardt, *Phys. Rev. A* **17**, 195 (1978) in the case of the $H^-2s2p^1P^o$ shape resonance.
- [28] C. A. Nicolaides, *Phys. Rev. A* **6**, 2078 (1972).
- [29] C. A. Nicolaides and D. R. Beck, *Phys. Lett. A* **65**, 11 (1978).
- [30] C. A. Nicolaides and D. R. Beck, *Int. J. Quantum Chem.* **14**, 457 (1978).
- [31] C. A. Nicolaides, Y. Komninos, and Th. Mercouris, *Int. J. Quantum Chem.* **S15**, 355 (1981).
- [32] Y. Komninos and C. A. Nicolaides, *Chem. Phys. Lett.* **78**, 347 (1981).
- [33] C. A. Nicolaides, H. J. Gotsis, M. Chrysos, and Y. Komninos, *Chem. Phys. Lett.* **168**, 570 (1990).
- [34] C. A. Nicolaides, in *Applied Many-Body Methods in Spectroscopy and Electronic Structure*, edited by D. Mukherjee (Plenum, New York, 1991).
- [35] U. Fano, *Phys. Rev.* **124**, 1866 (1961).
- [36] P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th ed. (Oxford University, New York, 1958), Chap. 8.
- [37] A. F. J. Siegert, *Phys. Rev.* **56**, 750 (1939).
- [38] G. Gamow, *Z. Phys.* **51**, 204 (1928).
- [39] The dc-field-induced transformation of the discrete spectrum into that of resonances has also been studied from the viewpoint of mathematical analysis based on the methods of Refs. [21,22] in Refs. [10–12].
- [40] A. M. Dykhne and A. V. Chaplik, *Zh. Eksp. Teor. Fiz.* **40**, 1427 (1961) [*Sov. Phys.—JETP* **13**, 1002 (1961)].
- [41] Th. Mercouris and C. A. Nicolaides, *J. Phys. B* **23**, 2037 (1990).
- [42] C. A. Nicolaides, Th. Mercouris, and N. Piangos, *J. Phys. B* **23**, L669 (1990).
- [43] Th. Mercouris and C. A. Nicolaides, *J. Phys. B* **24**, L57 (1991); **24**, L165 (1991).
- [44] M. Chrysos, Y. Komninos, Th. Mercouris, and C. A. Nicolaides, *Phys. Rev. A* **42**, 2634 (1990).
- [45] I. D. Petsalakis, Th. Mercouris, G. Theodorakopoulos, and C. A. Nicolaides, *J. Chem. Phys.* **93**, 6642 (1990).
- [46] G. D. Doolen, *Int. J. Quantum Chem.* **14**, 523 (1978).
- [47] R. Yaris, J. Bendler, R. A. Lovett, C. M. Bender, and P. A. Fedders, *Phys. Rev. A* **18**, 1816 (1978).
- [48] A. D. Isaacson, C. W. McCurdy, and W. H. Miller, *Chem. Phys.* **34**, 311 (1978).
- [49] C. H. Maier, L. L. Cederbaum, and W. Domcke, *J. Phys. B* **13**, L119 (1980).
- [50] O. Atabek and R. Lefebvre, *Chem. Phys. Lett.* **84**, 233 (1981).

- [51] J. N. L. Connor and A. D. Smith, *J. Chem. Phys.* **78**, 6161 (1983).
- [52] N. Moiseyev, P. R. Certain, and F. Weinhold, *Mol. Phys.* **36**, 1613 (1978).
- [53] S. -I. Chu, *J. Chem. Phys.* **72**, 4772 (1980).
- [54] M. Garcia-Sucre and R. Lefebvre, *Int. J. Quantum Chem.* **S20**, 541 (1986).
- [55] R. Lefebvre and H. S. Taylor, *J. Mol. Struct.* **199**, 327 (1989).
- [56] For a more complicated potential, x_0 is the point of maximum $V(x)$ after the last local minimum.
- [57] C. A. Nicolaides and Th. Mercouris, in *Atoms in Strong Fields*, edited by C. A. Nicolaides, C. W. Clark, and M. H. Nayfeh (Plenum, New York, 1990), p. 353.