Continuum orbitals, complex scaling problem, and the extended virial theorem

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A complex scale transformation of the time-independent Schrödinger equation leads to a symmetric eigenvalue problem containing both bound states and resonance (complex) eigenvalues as solutions. An extended virial theorem is stated, and its necessary fulfillment is pointed out. The latter, in conjunction with a symmetric stationary principle, allows for determination of resonance (complex) eigenvalues by means of elementary matrix manipulations. Application to the Stark effect in the hydrogen atom shows agreement with previous calculations based on numerical integration.

I. INTRODUCTION

Continuum orbitals and wave functions are needed in order to describe and analyze radiationless processes. The calculation of transition energies and moments between discrete states are well-known procedures, whether one uses a conventional wave-function picture or the recent powerful propagator technique.[1] When the continuum is involved, the ubiquity of nonquantization leads to a situation of a more difficult nature. It is our aim, however, to show in this paper that a simple extension of known stationary principles allows for a direct determination of resonance (complex) eigenvalues by means of standard matrix manipulations.

Before proceeding, we quote some earlier results. The complex-scaling problem emanates from the complex-coordinate method of Nuttall and Cohen.[2] The symmetric "Kohn type" variation principle that we will obtain here was derived and applied to a narrow-shape-resonance problem as well as the lowest ^1S resonance of H^- by Bain, Bardsley, Junker, and Sukumar.[3] In these and other related studies by Doolen,[4] Rescigno and Reinhardt,[5] and Reinhardt[6] it was found that resonance trajectories (as a function of rotation angle) "pause" near the true resonance. This observation, which also indicates stationarity in the total variation of the complex scale factor, prompts the formulation of a complex version of the virial theorem.[7] As we will see below, this condition (necessary but not sufficient) leads to important practical consequences. In all previously mentioned applications except Ref. 6, the considered Hamiltonians belong to the dilation analytic class[8,9] encompassing the theory of Aguilar, Balslev, and Combes.[8,9] The beauty of this idea is well described by Simon.[10] Reference 6, which contains a test of the complex-rotation method on the Stark effect in the hydrogen atom, differs from Refs. 3–5 in that the Stark Hamiltonian is *not* dilation analytic. The latter does, on the other hand, belong to Weyl's limit-point case,[11,12] assuring the existence of the concomitant spectral density from which the resonance can be extracted by analytic continuation. In the following, we will demonstrate how one arrives at the symmetric eigenvalue problem and the extended virial theorem. We will also devise a complex-scaling technique, in principle of general applicability, which we test on the Stark effect in the hydrogen atom.

II. AN EXTENDED VARIATIONAL PRINCIPLE

We start by writing down the time-independent Schrödinger equation for N (space-spin) degrees of freedom,

$$H(x_1, \ldots x_N)\psi(x_1, \ldots x_N) = \epsilon\psi(x_1, \ldots, x_N), \quad (1)$$

where H is the N-particle Hamiltonian (self-adjoint for real coordinates). We want to stress at this point that (1) also contains complex resonance solutions of the Gamow type provided appropriate boundary conditions are accepted. These are to be understood as formal solutions, to emphasize the fact that they do not satisfy the conventional boundary conditions, i.e.,, they are not square integrable.

By scaling each coordinate, i.e., letting $x_i' = \eta x_i$, where $\eta = \alpha e^{i\theta}$, the equation (1) has not changed except for the asymptotic behavior of the formal solutions just mentioned. In other words, the asymptotic properties of the solutions of (1) may depend dramatically on the phase of η. Our goal is hence to demonstrate that diverging outgoing waves may be treated on the same basis as ordinary bound-state solutions by a scale transformation of (1), applied in such a fashion that square integrability of the corresponding solution is assured. The price we have to pay for this convenience consists of the occurrence of a nonreal symmetric operator $H(\eta)$. As a consequence we need to derive an extended variation principle. Although this was suggested in Ref. 3, we will proceed here along differ-

ent lines. We introduce the notation

$$\psi(\eta) = \eta^{3N/2}\psi(\eta x_1, \ldots, \eta x_N), \tag{2}$$

$$H(\eta) = H(\eta x_1, \ldots, \eta x_N), \tag{3}$$

$$\epsilon(\eta) = \epsilon, \tag{4}$$

where $\epsilon(\eta)$, at least in some η domain, is independent of η, keeping in mind, however, the relationship between η and the boundary conditions as mentioned above. Reality of H for $\theta = 0$ leads to the following analyticity conditions obtained from Schwarz reflection principle:

$$\psi^*(\eta) = \psi(\eta^*), \tag{5}$$

$$H^*(\eta) = H(\eta^*), \tag{6}$$

$$\epsilon^*(\eta) = \epsilon(\eta^*). \tag{7}$$

These rules require an extremum principle of the symmetric type ($\bar{\psi}$ is a trial function):

$$\bar{\epsilon}(\eta) = \frac{\langle \bar{\psi}(\eta^*) | H(\eta) | \bar{\psi}(\eta)\rangle}{\langle \bar{\psi}(\eta^*) | \bar{\psi}(\eta)\rangle}. \tag{8}$$

[Note that the reality of approximate trial wave functions of Eq. (1) has previously been derived from the variational theorem.[13]]

We emphasize that the existence of (8) depends critically on the domain of η through the requirement of square integrability of $\psi(\eta)$. It is also possible to interpret (8) as a special case of a biorthogonal construction for a non-self-adjoint $H(\eta)$.

It is obtained that $\epsilon(\eta)$ is stationary for small variations around $\psi(\eta)$; i.e., writing $\bar{\psi}(\eta) = \psi(\eta) + \delta\psi(\eta)$, with $\langle \bar{\psi}(\eta^*) | \bar{\psi}(\eta)\rangle = 1$, we get

$$\bar{\epsilon}(\eta) - \epsilon(\eta) = \langle \delta\psi(\eta^*) | H(\eta) - \epsilon(\eta) | \delta\psi(\eta)\rangle. \tag{9}$$

Related variational principles have been derived in Refs. 14 and 15. We may also interpret the analysis in Ref. 16 by means of the present theory.

III. THE EXTENDED VIRIAL THEOREM AND ITS NUMERICAL IMPLEMENTATION

In order to find a practical way to obtain approximate resonance solutions from (8), we will make use of the extended virial theorem ($H = T + V$),

$$2\langle \psi(\eta^*) | T(\eta) | \psi(\eta)\rangle = \sum_{i=1}^{N} \langle \psi(\eta^*) | \eta \vec{r} \cdot \vec{\nabla}_{\eta r_i} V(\eta) | \psi(\eta)\rangle, \tag{10}$$

where the kinetic part of the Hamiltonian is denoted by $T(\eta x_1, \ldots, \eta x_N) = T(\eta)$. The proof is analogous to the ordinary one. In the same vein, the connection between the virial theorem and the variation principle follows.[18] As pointed out in Ref. 18, the exact solutions of (1), including concomitant scale transformations, satisfy (10) (provided appropriate η domains are considered). Condition (10) is a necessary but not a sufficient one, hence enforcement of (10) for approximate treatments provide, in addition to fulfillment of (8) and (9), also stationarity with respect to analytic changes in η. A very simple implementation of (8), (9), and (10) follows from a direct generalization of the successive scaling procedure of Nordling and Faulkner.[19] We indicate the procedure by the following scheme: (i) Choose $\gamma_0 = 1/\eta_0$, construct $H(\eta_0)$ according to (3), and solve the symmetric eigenvalue equation as a standard secular problem, where $\bar{\psi}_{\eta_0}(1)$ is expanded in a given basis $\bar{\psi}_{\eta_0}(1) = |\underline{h}(1)\rangle \underline{c}(\eta_0) = \sum_i h_i(1) c_i(\eta_0)$. (ii) Evaluate $\epsilon(\eta_0\eta_1)$, $\eta_1 = 1/\gamma_1$ as the "extended" expectation value (8) of $H(\eta_0\eta_1)$ with respect to $\bar{\psi}_{\eta_0}(1)$. (iii) Determine η_1 by requiring $\delta\epsilon(\eta_0\eta_1)/\delta\eta_1 = 0$. (iv) Replace γ_0 by $\gamma_0\gamma_1$, go back to (i), and proceed to determine $\gamma_2 = 1/\eta_2$, etc.; continue until $\gamma_i = 1/\eta_i \to 1$.

We will briefly comment on the steps (i)–(iv). If γ_0 is real, step (i) results in a standard Hermitian eigenvalue problem. If it is complex, we will deal with a complex symmetric secular equation. These secular problems arise from a biorthogonal construction, i.e., the bra ($\langle\ |$) entry will contain wave functions scaled with γ_0^* and the ket ($|\ \rangle$) entry the ones scaled with γ_0. Step (ii) will therefore lead to a polynomial in $\gamma = \eta^{-1}$ due to the simple homogeneity of the operators involved. In this case a particular scaling of the wave function is transferred to an equivalent inverse scaling of the operator, i.e., with respect to step (ii) we write

$$\langle \psi(\gamma_0^*\gamma_1^*) | H(1) | \psi(\gamma_0\gamma_1)\rangle = \langle \psi(\gamma_0^*) | H(\eta_1) | \psi(\gamma_0)\rangle. \tag{11}$$

Step (iii) contains the determination of the appropriate root γ_1 of the polynomial mentioned above, and step (iv) replaces γ_0 by $\gamma_0\gamma_1$ going back to step (i). It follows that convergence, i.e., γ_i and η_i go to unity, implies that the extended virial theorem (10) is satisfied. To avoid misunderstandings in the interpretation of this result, we find after the iteration procedure has converged (but not sooner!), that for $\gamma_0\gamma_1 \ldots \gamma_n = \gamma = 1/\eta$,

$$\epsilon(\eta) = \frac{\langle \psi_\eta^*(\gamma) | H(1) | \psi_\eta(\gamma)\rangle}{\langle \psi_\eta^*(\gamma) | \psi_\eta(\gamma)\rangle} = \frac{\langle \psi_\eta^*(1) | H(\eta) | \psi_\eta(1)\rangle}{\langle \psi_\eta^*(1) | \psi_\eta(1)\rangle} \tag{12}$$

with $\psi_\eta(1)$, according to step (i), obtained from a complex secular equation based on $H(\eta)$, i.e.,

$$\langle \underline{h}(1) | H(\eta) | \underline{h}(1)\rangle \underline{c}(\eta) = \epsilon(\eta)\underline{c}(\eta), \tag{13a}$$

$$\psi_\eta(1) = \underline{h}(1)\underline{c}(\eta). \tag{13b}$$

The equation underlying equality (12) is

$$\mathfrak{S}(1) = \langle \underline{h}(1) | \underline{h}(1)\rangle = \langle \underline{h}(\gamma) | \underline{h}(\gamma)\rangle = \mathfrak{S}(\gamma). \tag{14}$$

TABLE I. Stark resonances obtained from the complex-scaling–extended-virial theorem (algebraic method) as compared with those from Weyl's "complex-eigenvalue" theory (numerical integration) for various field strengths.

Field (a.u.)	Resonances (a.u.) Complex scaling; this work	Weyl's theory[12]
0.04	$-0.5037714-i0.191\times10^{-5}$	$-0.5037715-i0.195\times10^{-5}$
0.10	$-0.52742-i0.727\times10^{-2}$	$-0.52743-i0.727\times10^{-2}$
0.25	$-0.58575-i0.932\times10^{-1}$	$-0.58575-i0.940\times10^{-1}$

Since the converged result (12) by definition means fulfillment of steps (i)–(iii), we also obtain $d\bar{\epsilon}/d\eta = 0$. It should be pointed out that for a complete basis $|\underline{k}\rangle$, (13b) will be identical to (2). It is also important to note that our above described procedure depends on the starting point η_0 insofar as it has to be situated within the convergence radius of the considered resonance, which itself is most probably basis dependent. Regarding the question of the convergence, our experience and others (for the real case[19,21]) shows that it is quite easily obtained. If, however, the process is too slow and consequently very expensive, for instance as a consequence of the introduction of η-dependent basis elements, one can always try to locate stationary points directly from the knowledge of $d\bar{\epsilon}/d\eta$ in analogy with the real case described in Ref. 18.

In the execution of steps (i)–(iv) we have the option to choose our basis dependent or independent of η. In the latter case, no additional matrix elements need to be recalculated although the accuracy of the former should be higher due to the extra flexibility gained by the appropriate insertion of η in each step. Although a proper basis should contain "outgoing waves," negligence in this department was not of paramount importance in our test on the "Stark eigenvalues." The results of this calculation using 15–36 basis functions as described in Ref. 17 is displayed in Table I. Comparison is made with highly accurate Stark shifts and lifetimes by means of Weyl's complex eigenvalue theory.[12] Results of this study are also in perfect agreement with Refs. 6 and 23.

IV. CONCLUSIONS

We emphasize finally that $\psi(\eta)$ analytically continued up to the real η axis may turn ψ into a diverging "Gamow type" wave. From this follows that a resonance defined by analytic continuation of the Weyl-Titchmarsh m function[20] is identical with the present resonance associated with a symmetric "Hamiltonian," where the artificial phase difference between T and V via complex stretching of all coordinates leads to square integrable solutions. It is also interesting to note that the independent particle model allows for individual scaling of each separate coordinate.

In conclusion we stress the following points.

(a) With respect to the Stark effect in the hydrogen atom, we find that the extended virial theorem allows us to directly determine complex eigenvalues of the operator, which falls outside the dilation analytic class discussed by Aguilar, Balslev, and Combes.[8,9]

(b) From the computational point of view the virial theorem offers an efficient procedure for determining the appropriate complex scaling parameter η, such that stationarity in the symmetric "Kohn-like" principle is satisfied with respect to both linear and nonlinear variations. The simple version presented here further allows to accomplish nonlinear variations without recalculation of matrix elements.

(c) The general notion of an extended virial theorem also leads to important physical interpretations. Realizing that the analytic continuation of the whole Schrödinger equation is connected with the time-dependent problem via a Fourier-Laplace transformation[15] puts our model directly into a more general frame. A recent deperturbation model based on the Balslev-Combes dilation analytic theory applied to the $^1\Pi$ near degeneracy in SiO shows the importance of the virial theorem as an interpretative tool for spectroscopic considerations in connection with predissociation phenomena.[22]

Although our present computational effort is confined to a one electron system perturbed by an electric field, we believe that the present formulation may be suitable also for resonances in larger systems, thereby complementing existing trajectory procedures. Works on these lines are in progress.

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