Variational principle for quasibound states

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A minimum-variance principle for quasibound states is defined and utilized to investigate the corresponding energy resonances. The variational principle yields simultaneously a resonance energy E and a square-integrable wave function φ, such that minimum variance is obtained for arbitrary variations of a restricted class of square-integrable functions as well as with respect to variations of E. It is further shown that the optimum energy E_0 obtained from this method can simultaneously be written as an expectation value of the actual Hamiltonian with respect to $\varphi = \varphi(E_0)$. The example of the Stark effect in the hydrogen atom is studied. It is shown that the variationally obtained resonance energy coincides with the real part of the complex pole of the m function of Weyl, related to the Green's function of the system under consideration. It is also shown that the corresponding numerical application of the Rayleigh-Ritz variational method only gives meaningful results for field intensities below 0.06 a.u., as compared with the "exact" results of Hehenberger, McIntosh, and Brändas.

I. INTRODUCTION

The quantum-mechanical treatment of quasibound states is a difficult problem for several reasons. The first stems from the fact that these states are associated with energies in the continuous part of the spectrum, and this necessitates a scattering-theory point of view. At the same time, these states exhibit bound-state character, which causes complications in the scattering formulation. Although an application of conventional methods designed for bound states in this regard can give meaningful results, as explained by Kato,[1] the present situation is by no means satisfactory.[2] One of the most successful methods to deal with these problems is the Feshbach projection-operator technique.[3] This technique has been particularly employed in the treatment of autoionizing states of He and H⁻.[4]

An essential degree of justification in this application follows from the projection operator Q constructed by Hahn, O'Malley, and Spruch.[5] This situation changes, however, when more complicated systems are considered, and the search for new methods is needed.

Quasibound states also occur in such phenomena as predissociation, the Stark effect, or tunneling in general. All these phenomena provide examples of models which can be rigorously described to a high degree of accuracy. The fundamental quantity in this description is the spectral function $\rho(\omega)$. This function, or more specifically its first derivative, has been studied previously by means of the classical theory of second-order ordinary differential equations due to Weyl.[6,7] Although $d\rho/d\omega$ has poles on the real axis for energies corresponding to the discrete part of the spectrum, it is a bounded function for (real)

energies in the continuum (disregarding bound states imbedded in the continuum). In particular, Titchmarsh[8] has shown that the poles of the Green function (here related to $d\rho/d\omega$)[9] associated with the Schrödinger equation for the hydrogen atom in an electric field have moved down into the complex plane. In this case, the real part of the complex pole defines the resonance energy. It is clear, however, that a resonance appearing in a more complicated (than hydrogen) many-body system may not be subject to a direct analysis by means of Weyl's theory. Different techniques must then be employed. In this note we will study the occurrence of resonances via a variational principle that directly yields information about the real part of the complex pole. Since the Stark effect in the H atom has been studied in great detail, we have chosen this system for testing purposes.

II. SPECTRAL DENSITIES AND THE NATURE OF THE RESONANCE

Before proceeding we shall look at some relations which will help to reveal the nature of the resonance. We shall assume the resolution of the identity in terms of the Stieltjes integral

$$I = \int_{-\infty}^{+\infty} |\psi(\omega)\rangle \, d\rho(\omega) \langle \psi(\omega)| \, , \tag{1}$$

where

$$H\psi(\omega) = \omega\psi(\omega) \, . \tag{2}$$

In writing (1) as a Stieltjes integral we have the possibility of including both the discrete as well as the continuous part of the spectrum. In the following we will as a matter of convenience describe the continuum only; i.e., we will assume that $d\rho/d\omega < \infty$. Although specification of ρ is not

necessary at this stage, we can use several alternatives. If for the continuum states

$$\langle \psi(\omega) | \psi(\omega') \rangle = \delta(\omega - \omega') , \tag{3}$$

we simply obtain $d\rho(\omega) = d\omega$. On the other hand, if we define $\psi(\omega)$ as the regular solution of the radial Schrödinger equation, i.e., where the solution and its first derivative are 0 and 1 respectively at the origin, then it follows that $d\rho(\omega) = (d\rho/d\omega) d\omega$ where $\pi d\rho/d\omega$ is the imaginary part of the Weyl-Titchmarsh m coefficient.[6,7] Introducing the Weinstein-Aronszajn function,[14] where $\varphi \in L^2$ will be defined and discussed in Sec. III,

$$W(E + i\epsilon) = \langle \varphi | (E + i\epsilon - H)^{-1} | \varphi \rangle \tag{4}$$

we obtain, with the help of (1)

$$W(E + i\epsilon) = \int_{-\infty}^{\infty} \frac{|g(\omega)|^2 d\rho(\omega)}{(E + i\epsilon - \omega)} , \tag{5}$$

where

$$g(\omega) = \langle \varphi | \psi(\omega) \rangle . \tag{6}$$

Note that the weighted distribution $|g(\omega)|^2 d\rho(\omega) = d\bar\rho(\omega)$ gives a third choice of a possible spectral density, provided ρ has zero measure on $\Omega_0 = \{\omega | g(\omega) = 0\}$. Taking the limit $\epsilon \to \pm 0$, one arrives at

$$\lim_{\epsilon \to \pm 0} W(E + i\epsilon) = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\bar\rho(\omega)}{E - \omega} \mp i\pi \left(\frac{d\bar\rho}{d\omega}\right)_{\omega = E} , \tag{7}$$

where $\mathcal{P}$ indicates the principal value of the integral. From Ref. 11, we have the relation

$$W(\mathcal{E}) = \frac{1}{\mathcal{E} - f(\mathcal{E})} , \tag{8}$$

in which $f(\mathcal{E})$ stands for the Löwdin bracketing function, defined by

$$f(\mathcal{E}) = \langle \varphi | H | \varphi \rangle + \langle \varphi | HP(\mathcal{E} - PHP)^{-1}PH | \varphi \rangle , \tag{9}$$

$$P = 1 - | \varphi \rangle \langle \varphi | . \tag{10}$$

Using the resolution of P for some convenient $d\rho_P(\omega)$

$$P = \int_{-\infty}^{\infty} | \psi_P(\omega) \rangle d\rho_P(\omega) \langle \psi_P(\omega) | , \tag{11}$$

$$PHP\psi_P(\omega) = \omega\psi_P(\omega) , \tag{12}$$

we can write

$$f(\mathcal{E}) = \langle \varphi | H | \varphi \rangle + \int_{-\infty}^{\infty} \frac{|g_P(\omega)|^2}{\mathcal{E} - \omega} d\rho_P(\omega) \tag{13}$$

with

$$g_P(\omega) = \langle \varphi | H | \psi_P(\omega) \rangle . \tag{14}$$

Again taking the limit $\epsilon \to \pm 0$, one gets

$$f(E) = \langle \varphi | H | \varphi \rangle + \mathcal{P} \int_{-\infty}^{\infty} \frac{d\bar\rho_P(\omega)}{E - \omega} \mp i\pi \left(\frac{d\bar\rho_P}{d\omega}\right)_{\omega = E} , \tag{15}$$

where we have absorbed $g_P(\omega)$ into $d\bar\rho_P(\omega)$, i.e.,

$$|g_P(\omega)|^2 d\rho_P(\omega) = d\bar\rho_P(\omega) . \tag{16}$$

We are now in a position to discuss the definition of a resonance. Since a bound state would show up as a real pole of $W(\mathcal{E})$ in (7), or in its imaginary part $\pi d\bar\rho/d\omega$, a quasibound state or resonance defined by a complex pole of $W(\mathcal{E})$ in the vicinity of the real energy axis, would appear as a sharp peak in $d\bar\rho/d\omega$, as ω passes a certain energy region. At the same time the principal-value integral taken as a function of E changes sign (passes through zero) in the same range of energy. It would then be natural to define the resonance E_r as the energy which satisfies

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{d\bar\rho(\omega)}{E_r - \omega} = 0 \tag{17}$$

Equating $\text{Re}\{W(E_r)\} = 0$ from (7), identical to (17), with the relation (8), where $f(E_r)$ will be obtained from (15), we obtain, provided the imaginary part of $f(E_r)$ is different from zero,

$$E_r = \langle \varphi | H | \varphi \rangle + \mathcal{P} \int_{-\infty}^{\infty} \frac{d\bar\rho_P(\omega)}{(E_r - \omega)} \tag{18}$$

which together with the interrelationship between $W(\mathcal{E})$ and $f(\mathcal{E})$ [Eq. (8)] prompts the following formula:

$$-\text{Im} f(E_r) = \epsilon_r = \pi \left(\frac{d\bar\rho_P(\omega)}{d\omega}\right)_{\omega = E_r} = 1 \bigg/ \pi \left(\frac{d\bar\rho}{d\omega}\right)_{E_r} . \tag{19}$$

Note that Eqs. (18) and (19) correspond to a separate evaluation of the real and imaginary parts of $\mathcal{E} = f(\mathcal{E})$, without taking their interdependence into account. If $f(\mathcal{E})$ varies slowly around E_r, it is easily deduced that $d\bar\rho/d\omega$ is a Lorentzian with a complex pole at $\mathcal{E} = E_r - i\epsilon_r$. In general it may of course happen that $d\bar\rho/d\omega$ is asymmetric and as a result the dependence between the real and imaginary parts of $f(\mathcal{E})$ has to be taken into account while solving for $\mathcal{E} = f(\mathcal{E})$.[15] As an example of asymmetry we mention the Stark effect in the hydrogen atom for high fields.[7]

III. A VARIATIONAL PRINCIPLE

It is well known that upper bounds to an eigenvalue are given by the Rayleigh-Ritz method and the Hylleraas-Undheim theorem.[10] Lower bounds are in general more difficult to obtain although

developments based on Löwdin's bracketing function[11] are progressing. The most general lower bound is given by Weinstein[12] in terms of the width $\sigma(\langle\langle H\rangle\rangle)$ defined by

$$\sigma(\langle\langle H\rangle\rangle) = \langle H^2\rangle - \langle H\rangle^2 = \langle (H-\langle H\rangle)^2\rangle , \qquad (20)$$

where the average is taken with respect to a trial function. Russek et al.[13] have analyzed the bounding properties of σ in connection with the energy levels and lifetimes of autoionizing states. Within the framework of Feshbach's projection operator Q a resonance is defined as the eigenstate of QHQ provided the level shift can be neglected. In order to discuss this situation, we shall consider the quantity (E in the continuum)

$$\sigma(E) = \langle\varphi| (H - E)^2|\varphi\rangle , \quad \langle\varphi|\varphi\rangle = 1 , \qquad (21)$$

where $\varphi = \varphi(E)$ is a square-integrable trial function depending on E. The wave function φ, which will be determined from $\delta(\sigma(E)) = 0$ for E fixed, will presumably mimic the inner part of the true solution $\psi(E) \notin L^2$ of the Schrödinger equation (2). The actual choice of trial functions will be discussed below. The minimization of $\sigma(E)$ has been used by a number of people, see e.g. Bardsley et al.[16]; see also Ref. 17. Extensions of the Rayleigh-Ritz principle to scattering problems have furthermore attracted considerable attention, but we will not discuss these aspects here.

The minimization of $\sigma(E)$, with E fixed, has a very simple solution. Considering linear variations in the manifold $|\underline{h}\rangle$, i.e. assuming

$$\varphi(E) = |\underline{h}\rangle \underline{c}(E) \qquad (22)$$

we obtain immediately a secular equation from

$$\delta(\sigma(E)) = \langle\delta\varphi| (H - E)^2|\varphi\rangle = 0 , \qquad (23)$$

where the lowest root yields the minimum of $\sigma(E)$, for E specified.

The following theorem can now be proved: If φ is fixed and $\langle H\rangle = \langle\varphi|H|\varphi\rangle$, then

$$\sigma(\langle\langle H\rangle\rangle) \leqslant \sigma(E) . \qquad (24)$$

The proof follows easily from considering the quadratic form

$$E^2 - 2E\langle H\rangle + \langle H^2\rangle = \sigma(E) \geqslant 0 , \qquad (25)$$

which attains its lowest value for $E = \langle H\rangle$.

Here we note in passing that $\sigma(E)$ can be made arbitrarily small by enlarging the manifold $|\underline{h}\rangle$. This follows directly from the properties of the Hilbert space.

In order to trace the resonance, we vary the energy in the continuous region of the spectrum until the value of E which minimizes $\sigma(E)$ is found. In this process we get $\varphi(E)$ automatically by varying its linear and nonlinear parameters for

each given E. Suppose that a minimum is obtained for some $E = E_0$, i.e.,

$$\sigma(E_0) = \langle\varphi(E_0)| (H - E_0)^2|\varphi(E_0)\rangle = \min . \qquad (26)$$

Then, if $\sigma(E_0)$ is an absolute minimum for variations $\delta(\varphi(E))$ within $|\underline{h}\rangle$ manifold, i.e., $\sigma(E_0) \leqslant \sigma(E)$ for all E or interval containing $\langle H\rangle$, Eq. (24) shows that $\sigma(E_0) = \sigma(\langle\langle H\rangle\rangle)$ and

$$E_0 = \langle\varphi(E_0)|H|\varphi(E_0)\rangle . \qquad (27)$$

In other words by minimization of $\|(H - E)\varphi\|^2$ we have obtained an approximate square-integrable solution to Eq. (2) such that the mean energy E_0 also yields minimum variance.

Let us now consider the definition of $\varphi(E_0)$ in relation to eigenstates of QHQ. If we let Q denote the projection operator onto the manifold $|\underline{h}\rangle \equiv \{h_i\}_{i=1}^N$, we have that

$$\langle\varphi(E_0)|QHQ - E_0|\varphi(E_0)\rangle = 0 \qquad (28)$$

but not necessarily

$$\langle\varphi(E_0)| (QHQ - E_0)^2|\varphi(E_0)\rangle = 0 \qquad (29)$$

or

$$QHQ\,\varphi(E_0) = E_0\varphi(E_0) . \qquad (30)$$

Using Russek's notation we can write

$$\sigma(E_0) = \sigma_Q(E_0) + \sigma_P(E_0) \qquad (31)$$

with

$$\sigma_Q(E_0) = \langle\varphi(E_0)| (QHQ - E)^2|\varphi(E_0)\rangle , \qquad (32)$$

$$\sigma_P(E_0) = \langle\varphi(E_0)| (QHP)PHQ|\varphi(E_0)\rangle . \qquad (33)$$

Instead of trying to get $\sigma_Q = 0$ by solving the eigenvalue equation for QHQ exactly, we are instead obtaining a direct minimization of the total width $\sigma(E)$. Although that may give the result that $\sigma_Q(E) \neq 0$, we still retain exactly

$$E_0 = \langle\varphi(E_0)|H|\varphi(E_0)\rangle , \quad \langle\varphi(E_0)|\varphi(E_0)\rangle = 1 . \qquad (34)$$

Comparing Eq. (27) with the resonance behavior previously discussed [Eq. (18)], we can conclude the following. If for the choice $\varphi = \varphi(E_0) \equiv \varphi_0$ in (18), the principal-value integral can be neglected in comparison to $\langle\varphi_0|H|\varphi_0\rangle$, since we have indeed minimized a mean-square deviation, then we can write

$$E_r = \langle\varphi_0|H|\varphi_0\rangle = E_0 . \qquad (35)$$

It will be shown in the next section that this is actually the case and that we may directly include the level shift by a proper choice of the reference function. This appears to be the optimal φ from the manifold spanned by $|\underline{h}\rangle$, determined through a minimization of the width $\sigma(E)$.

IV. NUMERICAL RESULTS AND DISCUSSION

A hydrogen atom placed in an electric field has been chosen for testing purposes. The resonance energies have been calculated for field intensities ranging from 0.01 to 0.25 a.u.

The manifold $|\underline{h}\rangle$ used for the determination of the reference function φ_0 was spanned by 15 Slater-type functions, five of them being of s type, four of p type, etc., ending with one function of g type.

The reference function φ_0 was chosen to be the one which minimizes the width $\|(H - E)\|^2 \equiv \sigma(E)$, $\varphi \in |\underline{h}\rangle$. The minimization process consisted both of linear and nonlinear variations, the latter being the variation of the exponential parameter α in the STO's. It turns out that nonlinear effects are important for field intensities stronger than 0.1 a.u., whereas linear variations alone give good results for weaker fields; see Figs. 1 and 2. The reference curve (broken line) on both figures is based on data obtained by Hehenberger et al.[7] from the real component of the complex pole of Weyl's m function. The variational approach described in this note is presented in Table I and in Fig. 3.

We have also calculated the resonance energies by means of the conventional Rayleigh-Ritz method. The resulting curve, as well as the reference curve due to Ref. 7, is shown in Fig. 3 for comparison. We notice that the resonance energies obtained variationally as described here agree with those obtained in Ref. 7. The agreement holds for the whole range of field intensities considered (i.e., 0.01–0.25 a.u.), and the largest discrepancy between those two methods in this range

FIG. 2. Same as for Fig. 1, but with $\alpha = 0.75$.

does not exceed 5×10^{-4} a.u.

We observe also that the ground state branch obtained from the conventional Rayleigh-Ritz method in our case gives meaningful results for field intensities below 0.06 a.u. As is well known this method is not strictly applicable for an unbound Hamiltonian. Still the rigor can be maintained in the sense of Kato[1] that the outer part of the potential could sometimes be ignored in favor of the interior part, and hence L^2 functions may somehow represent the resonant wave function. The minimum variance principle, as discussed here, seems to extend the domain of applicability for which these considerations are valid.

Our investigation of the minimum variance method as applied to the determination of quasibound states may essentially be summarized in three statements.

(a) The optimization of φ with respect to linear and nonlinear parameters for a fixed E yields $\varphi = \varphi(E)$ uniquely. Trial functions are chosen
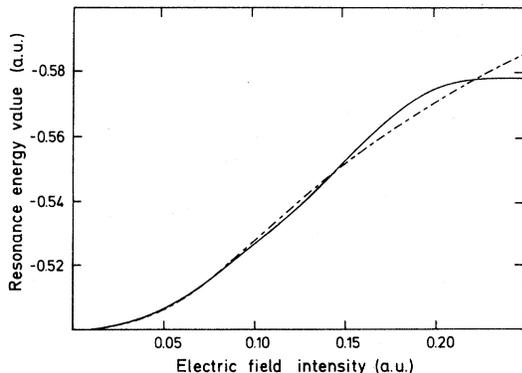

FIG. 1. Effect of nonlinear variations is demonstrated. Their importance for field intensities higher than 0.1 a.u. is shown; for field intensities less than 0.1 a.u. the effect of nonlinear variations is insignificant. The exponential parameter $\alpha = 1.0$. See Sec. IV for further discussion.
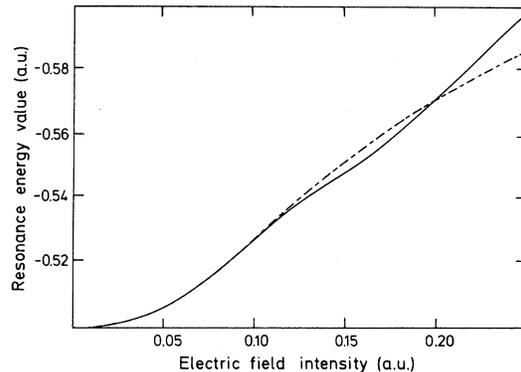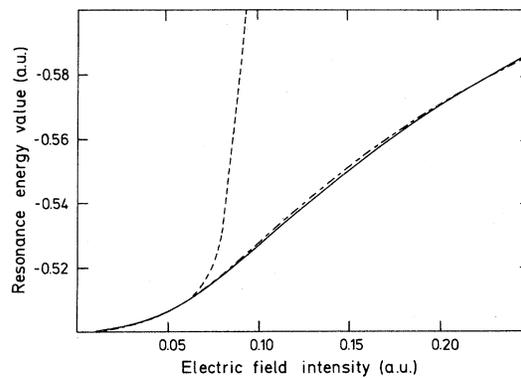

FIG. 3. Resonance energies obtained by (a) the variational method described in text (solid line); (b) Weyl's m-function method, after Ref. 7 (irregularly broken line); (c) ordinary Rayleigh-Ritz variational method (regularly broken line).

TABLE I. Resonance energies shown in Fig. 3, and values of the exponential parameter α optimized for the case (a).

Field intensity (a.u.)	α	Resonance energy (a)	Resonance energy (b)	Resonance energy (c)
0.01	1.0	−0.500 225 6	−0.500 225 6	−0.500 225 6
0.02	1.0	−0.500 909 2	−0.500 909 2	−0.500 909 2
0.03	1.0	−0.502 074 0	−0.502 074 2	−0.502 074 0
0.04	1.0	−0.503 767	−0.503 771	−0.503 768
0.05	1.0	−0.506 075	−0.506 105	−0.506 090
0.06	1.0	−0.509 145	−0.509 203	−0.509 295
0.07	1.0	−0.513 091	−0.513 077	−0.514 427
0.08	1.0	−0.517 631	−0.517 561	−0.531 256
0.09	1.0	−0.522 085	−0.522 415	−0.580 912
0.10	0.8345	−0.526 945	−0.527 432	−0.639 315
0.13	0.9714	−0.541 418	−0.542 156	−0.821 293
0.16	1.0817	−0.554 681	−0.555 406	−1.006 825
0.20	1.2041	−0.570 173	−0.570 529	−1.256 903
0.25	1.3313	−0.586 554	−0.585 757	−1.572 027

that are square integrable. Varying E as the next step, obtaining minimum variance at $E = E_0$, provides, in addition, expectation value character, i.e.,

$$E_0 = \langle \varphi(E_0) | H | \varphi(E_0) \rangle, \quad \sigma(E_0) = \text{a minimum}. \quad (36)$$

(b) Accurate determination of resonances for the Stark effect in the hydrogen atom has recently been obtained for very high field strengths (above 0.12 a.u.) by Hehenberger et al.[7] This made possible a critical test of the minimum variance method as applied to quasibound states with linewidth's of considerable magnitudes as well as asymmetric shapes.

(c) Our results show that the application of the minimum variance principle as presented here, leads to a correct numerical description of the real part of the actual resonance as a function of the field strength.

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