PHYSICAL REVIEW A VOLUME 17, NUMBER 1 JANUARY 1978

Connection between configuration-mixing and quantum-defect treatments

U. Fano

Department of Physics, University of Chicago, Chicago, Illinois 60637

(Received 10 June 1977)

Alternative formulations of atomic problems are connected in terms of the Green's function for the radial motion of a single electron in an effective potential field. The quantum-defect theory (QDT) represents an electron outside an ion by a Coulomb function with a phase shift contributed by the additional interactions that prevail inside the ion core. We interpret the phase-shifted portion of this radial function as arising from the application of a Green's function propagator to the short-range operator that represents the coupling to other channels of the electron + ion system. The alternative representation of the same radial function, as a superposition of zero-order functions for configurations with different energies, differs only by having the same Green's function expanded in a set of zero-order eigenfunctions. This analysis of configuration mixing leads to a reformulation of reaction matrices which extends the initial QDT treatment of bound states.

I. INTRODUCTION

Quantum-defect treatments of atomic and molecular processes are finding increasing application, but their connection with more general and familiar treatments does not seem to have been described adequately. This circumstance has emerged particularly in a recent and extensive treatment of the excitation and ionization of the H_2 molecule, which also outlines an extension toward dissociation.[1] Reference 1 transforms the familiar formulation of the full H_2 Hamiltonian into an application of quantum-defect procedures, without describing the transformation in full detail.

Seaton's original formulation of the multichannel quantum-defect theory (MQDT)[2] rests on a truncated close-coupling expansion of the many-particle eigenfunction, and on extrapolation of a reaction matrix from the continuous to the discrete spectrum. Some of the later applications of MQDT have been frankly phenomenological.[3] Here we derive, instead, the MQDT from a configuration-mixing point of view, namely, by representing eigenfunctions of the full Hamiltonian as superpositions of eigenfunctions of an approximate Hamiltonian. The derivation is somewhat laborious but it may clarify concepts of the MQDT and remove the limitations indicated above. Section I outlines the background of the problem and the main results; details follow in separate sections for the continuous and discrete spectra.

One key idea of the MQDT is to regard a many-electron system as separated into a core and an escaping electron, when the radial distance r of an electron from the center of the core has attained a sufficient value r_0. Wave functions of core + electron are then represented in the range $r \geqslant r_0$ by a close-coupling expansion

$$\Psi = \sum_i [F(\epsilon_i, r)\cos\delta_i - G(\epsilon_i, r)\sin\delta_i]\Phi_i B_i \;. \quad (1)$$

Here the expression in brackets is the radial wave function of the escaping electron, Φ_i represents a coupled wave function of the orbital and spin coordinates of this electron and of the core in its ith stationary state, and the coefficients B_i identify a particular superposition of channels. Different channel functions Φ_i may include the same stationary state of the core; hence energy parameters ϵ_i and ϵ_j of Eq. (1) with different indices may be equal. The variable of the radial function r indicates the distance of the electron *farthest* from the core's center; this specification removes the need for explicit antisymmetrization. The radial function in Eq. (1) is a general standing-wave solution of the radial equation for an electron moving in the field generated by the core at $r > r_0$, which is generally Coulombic and excludes exchange effects. This radial function is represented as the superposition of two particular solutions, F and G, with G lagging in phase by 90° with respect to F. The two functions (F, G) are usually defined also within the core, i.e., for $r_0 \geqslant r \geqslant 0$, as wave functions of a Coulomb field or, alternatively, of a more realistic atomic field which may include a nonlocal potential that represents exchange; in either case, F is the function regular at $r = 0$. The functions F and G are normalized per unit energy and ϵ_i represents the energy of the escaping electron, i.e., the difference of the total energy E of the system and of the energy level E_i of the core in the state Φ_i. The parameters δ_i are provided by a separate calculation of channel coupling at $r \leqslant r_0$ or by analysis of experimental data.

Seaton's original form of the MQDT assumes initial knowledge of a finite (i.e., truncated) set of functions Φ_i and of the corresponding core energies E_i. For total energies E in excess of all E_i, the Schrödinger equation of electron + core reduces then to a system of coupled equations for radial functions $f_i(\epsilon_i, r)$, regular at $r=0$, with $\epsilon_i = E - E_i$. [Here again, as in Eq. (1), energies ϵ_i and ϵ_j with different indices may be equal.] Each f_i is represented for $r \geq r_0$ as a superposition of Coulomb functions F and G. A general energy eigenfunction is then represented for $r \geq r_0$ by Eq. (1), in which the coefficients

$$B_i \cos\delta_i = C_i \tag{2}$$

remain free while

$$B_i \sin\delta_i = -\pi \sum_j K_{ij}(E) C_j\,, \tag{3}$$

with the reaction matrix K_{ij} determined by the solution of the coupled radial equations for $r \leq r_0$. The K matrix is then extrapolated to energies E lower than one or more of the core energies E_i, whereby some of the escape energies ϵ_i become negative, meaning that the corresponding channels are closed. The requirement that $f_i(\epsilon_i, r)$ remain finite at $r=\infty$ in the closed channels imposes linear restrictions on the coefficients C_i. When all channels are closed, these restrictions are compatible only for discrete energy eigenvalues E. Reference 3 has described applications of the MQDT from a more flexible point of view, which is compatible with Seaton's approach, or alternatively with empirical fitting of the core energies E_i and of the reaction matrix $K_{ij}(E)$, or with calculation of K_{ij} by the R-matrix procedures which are confined to the finite volume of the core.[4]

Configuration-mixing treatments follow instead the traditional approach of separating the Hamiltonian of the whole system into two terms, $H = H_0 + V$, and of constructing eigenfunctions of H as superpositions of a complete set of eigenfunctions of H_0. To maintain a degree of parallelism with Seaton's approach we indicate the eigenfunctions of H_0 by $\mathcal{A}\{f_{in}(r)\Phi_i\}$—where $\mathcal{A}$ stands for the antisymmetrization that is required for r values within the core—i.e., we set $(H_0 - E_i - \epsilon_{in})\mathcal{A}\{f_{in}\Phi_i\} = 0$. The constructional definition of f_{in} and Φ_i differs, however, here and in the MQDT. In the elementary form of configuration mixing, Φ_i is constructed from a complete orthonormal set of independent particle wave functions and $f_{in}(r)$ is itself the radial part of one of these functions; the set of Φ_i is also implicitly complete, rather than truncated. Correlations may be built initially in the Φ_i by superposition of Slater determinants in the case of configuration mixing, while the MQDT places fewer restrictions on the Φ_i. We write the equation for the radial functions f_{in} as

$$h_i(r) f_{in}(r) = \epsilon_{in} f_{in}(r)\,, \quad 0 \leq r \leq \infty\,. \tag{4}$$

An index i has been appended here to the Hamiltonian to allow for modifications of the elementary procedure, in which the optical potential—including exchange—depends on the core state[5]; any such modification should, however, preserve the orthonormality of the $\mathcal{A}\{f_{in}\Phi_i\}$. The eigenvalues ϵ_{in} of Eq. (4), and the corresponding eigenvalues $E_i + \epsilon_{in}$ of H_0, are of course unrestricted to allow the mixing of configurations of different energy. The desired eigenfunctions of H are then represented by

$$\Psi = \sum_i \sum_n D_{in} \mathcal{A}\{f_{in}(r)\Phi_i\}\,, \tag{5}$$

where each $\sum_n$ generally extends over a discrete and continuous spectrum and the coefficients D_{in} obey a system of equations

$$\epsilon_{in} D_{in} + \sum_j \sum_m (in|V|jm) D_{jm} = D_{in}\epsilon_i \tag{6}$$

with $\epsilon_i = E - E_i$. (We consider in this paper eigenfunctions of H_0 and of H that are eigenfunctions of the total angular momentum and are of the standing wave type.)

The main purpose of this paper is to derive the MQDT representation (1) of a wave function from the more general, configuration-mixing expansion (5). The derivation consists essentially of two remarks drawn from the Green's function treatment of scattering theory[6]:

(a) When Eq. (6) is solved in terms of a reaction matrix K, the summation over n in Eq. (5) can be expressed in terms of the eigenfunction expansion of the Green's function of the radial Hamiltonian $h_i(r)$,

$$\mathcal{G}_i(\epsilon_i; r, r') = \sum_n f_{in}(r)(\epsilon_i - \epsilon_{in})^{-1} f_{in}(r')\,. \tag{7}$$

The applications to atomic problems utilize the "two-potential" approach[6] of including a part of the interaction in the Hamiltonian $h_i(r)$ and the rest in the operator V of Eq. (6), and envisage the direct numerical solution of Eq. (4) and of the K matrix form of Eq. (6).

(b) The summation over configurations n of different energies is then carried out simply by replacing the expanded form (7) of the Green's function by its alternative form in terms of the regular and irregular solutions of Eq. (4) at the energy ϵ_i that are 90° out of phase,

$$\mathcal{G}_i(\epsilon_i; r, r') = \pi g_i(\epsilon_i, r) f_i(\epsilon_i, r')\,, \quad r > r'\,. \tag{8}$$

[In Eq. (8) the coefficient is set to π by the normalization of f and g per unit energy and by the phase of g lagging that of f; these conventions differ from those of Ref. 6.]

The application of these remarks is straightforward as long as one deals only with continuous spectra, i.e., with positive values of ϵ_i (Sec. II). In practice, however, the study of electron + core systems generally involves negative values of ϵ_i, corresponding to closed channels. This circumstance will lead us, in Sec. III, to modify the procedure for solving Eq. (6) in terms of a K matrix, in order to avoid the singular behavior of this matrix in the presence of closed channels. Seaton has avoided these singularities by extrapolating to negative ϵ_i the K matrix calculated for a truncated set of channels with all $\epsilon_i > 0$. He points out that extrapolation is in fact dependable over the most relevant range of 3–5 eV below a threshold. On the other hand it may be worthwhile to develop an alternative that avoids numerical extrapolations as well as truncations of the set of channels Φ_i which are realistic only when the spectrum of threshold energies E_i shows a major gap. Properties of the Green's functions for a discrete spectrum will in fact permit us to construct a "smoothed out" reaction matrix $K^{(s)}$ which is equivalent to Seaton's but can be calculated for closed channels without resorting to extrapolation. The matrix $K^{(s)}$ is substantially equivalent to an R matrix.

II. CONFIGURATION MIXING IN THE CONTINUUM

Consider initially energies E in excess of all E_i, i.e., such that all $\epsilon_i > 0$, as in Seaton's treatment. The linear system, Eq. (6), is then singular because the coefficient of D_{in}, namely, $\epsilon_i - \epsilon_{in}$, may vanish. There results a singularity of the solutions D_{in} which may be represented by the superposition of two terms. One term equals $\delta(\epsilon_i - \epsilon_{in})C_i$, where C_i is a coefficient discussed below; its contribution to the wave function (5) does not admix configurations of different energies,

$$\sum_n \mathcal{A}\{f_{in}(r)\Phi_i\}\delta(\epsilon_i - \epsilon_{in})C_i = \mathcal{A}\{f_i(\epsilon_i, r)\Phi_i\}C_i\,. \tag{9}$$

[We have introduced in Eq. (9), as in Eq. (8), the symbol $f_i(\epsilon_i, r)$ to indicate the $f_{in}(r)$ with $\epsilon_{in} = \epsilon_i$, i.e., "on the energy shell."] The other term represents the mixing of configurations of the same channel i but with energies other than ϵ_i (i.e., "off the energy shell"); the energy ϵ_i is *excluded* here from the mixing by restricting the superposition through the principal part integration symbol P. Solution of Eq. (6) for standing-wave boundary conditions have then the form[7]

$$D_{in} = \delta(\epsilon_i - \epsilon_{in})C_i + P(\epsilon_i - \epsilon_{in})^{-1} \times \sum_k (f_{in}\Phi_i|K(E)|f_k(\epsilon_k)\Phi_k)C_k\,. \tag{10}$$

The coefficients of the second—configuration mixing—term of Eq. (10) constitute a column of off-shell elements of the reaction matrix K; we have replaced here the row indices "in" of this matrix by the fuller description of a base function, $f_{in}\Phi_i$. The channel coefficients C_i, akin to those of Eqs. (2) and (3), are not determined by the Schrödinger equation (6) but serve to identify one eigenfunction of a degenerate manifold, usually in terms of boundary conditions; this paper does not concern itself with their determination. The K-matrix elements, instead, replace the D_{in} as the parameters to be determined by Eq. (6). When Eq. (10) is substituted into (6), multiplication of D_{in} by $\epsilon_i - \epsilon_{in}$ eliminates the δ-function term and cancels the pole of the second term. There results a linear combination of coefficients C_k set equal to zero, a condition which is met by setting to zero the coefficient of each C_k. Thus one obtains the Lippmann-Schwinger equation for the K matrix [Eq. (2.23), Ref. 6],

$$\begin{aligned}(f_{in}\Phi_i|K(E)|f_k(\epsilon_k)\Phi_k) &= (f_{in}\Phi_i|V|f_k(\epsilon_k)\Phi_k) \\ &\quad + \sum_j \sum_m (f_{in}\Phi_i|V|f_{jm}\Phi_j)P(\epsilon_j - \epsilon_{jm})^{-1} \\ &\quad \times (f_{jm}\Phi_j|K(E)|f_k(\epsilon_k)\Phi_k)\,.\end{aligned} \tag{11}$$

This system of coupled integral equations can be reduced to a finite algebraic system by taking the $\sum_m$ over a discrete mesh and by truncating it at large ϵ_{jm}; numerical solutions of this system have been obtained for particular applications.[8]

What matters for us is that the mixing of configurations can be described in terms of a K matrix which is calculable, and that this description is obtained by substituting Eq. (10) into (6). The resulting wave function is

$$\Psi = \sum_i \Phi_i\Big(f_i(\epsilon_i, r)C_i + \sum_n f_{in}(r)\frac{P}{\epsilon_i - \epsilon_{in}} \times \sum_j (f_{in}\Phi_i|K(E)|f_j(\epsilon_j)\Phi_j)C_j\Big)\,. \tag{12}$$

The decisive step consists now of noticing that the $\sum_n$ in Eq. (12) operates on the same set of n-dependent factors as the $\sum_n$ on the right-hand side of Eq. (7), if we allow for the following differences of notation: The P symbol is generally implied but not explicitly included in the expansion (7) of a Green's function[6]; on the other hand the variable r' of the last factor of Eq. (7) is only implied—and integrated over—in the definition of the K-matrix element. The effect of *configuration mixing* in the ith channel can thus be represented in *terms of the Green's function* $\mathcal{G}_i$ of Eq. (7), evaluated for the single on-shell energy ϵ_i, and of the operator K, *without further resort* to explicit superposition of wave functions $f_{in}(r)$ for all different energies ϵ_{in}. This fact is familiar in analytic manipulations of scattering theory; we apply it here in the context of a Green's function of the single-particle Hamiltonian h_i with an unspecified optical potential.

Our application consists then of replacing, in Eq. (12), the expanded form (7) of the Green's function by the form (8) which involves only radial functions on the energy shell. The restriction on Eq. (8), namely $r > r'$, is particularly appropriate to our aim of studying the wave function for radial distances larger than the core radius r_0. This restriction provides us in fact with an operational definition of r_0; this core radius must exceed all radial distances r' at which the interaction V and the corresponding reaction operator K are nonzero. [Recall, however, that the optical potential of the core need not vanish at $r > r_0$, because this potential is included in $h_i(r)$, i.e., in the portion H_0 of the Hamiltonian. We are only assuming that the aggregate effect of the *short range* interactions V, represented by K, is confined to $r' < r_0$.] Replacing then in Eq. (12) the expression (7) of $\mathcal{G}_i$ by the expression (8), we have

$$\Psi = \sum_i \Phi_i\Big(f_i(\epsilon_i, r)C_i + \pi g_i(\epsilon_i, r) \times \sum_j (f_i(\epsilon_i)\Phi_i|K(E)|f_j(\epsilon_j)\Phi_j)C_j\Big), \quad r \geq r_0. \tag{13}$$

All the reaction matrix elements in this expression belong now to the submatrix pertaining to states on the energy shell; these elements can be indicated more briefly by $K_{ij}(E)$, as in Eq. (3), since the rows and columns of the submatrix are labeled adequately by the channel indices (i, j). Thereby Eq. (13) reduces to

$$\Psi = \sum_i \Phi_i\Big(f_i(\epsilon_i, r)C_i + \pi g_i(\epsilon_i, r)\sum_j K_{ij}(E)C_j\Big), \quad r \geq r_0. \tag{14}$$

The configuration-mixing wave function Ψ has thus been reduced to coincide, at least in essence, with the quantum-defect wave function (1), as complemented by Eqs. (2) and (3). More specifically, Eqs. (1) and (14) coincide altogether for $r > r_0$ if the pair of radial functions (F, G) of Eq. (1) obeys the equation $[h_i(r) - \epsilon_i]y(r) = 0$ not only for $r > r_0$, as specified by their definition, but also for $r < r_0$. If this equation is obeyed only for $r > r_0$, F and G must nevertheless be represented in this range as superpositions of (f_i, g_i); Eqs. (1) and (14) are then brought to coincide by appropriate adjustments of Eqs. (2) and (3).

In conclusion, we stress the critical role played in this section by the inhomogeneous Eq. (11). Its solution, combined with later use of Green's function properties, enables us to eliminate explicit consideration of the mixing of off-the-shell configurations, by embodying the effect of this mixing in the on-the-shell submatrix $K_{ij}(E)$. This simplification rests, of course, on the fact that we have confined our aim to a description of the wave function for $r > r_0$ only.

III. DISCRETE LEVELS AND DETACHMENT THRESHOLDS

Substantial adaptation of the procedure of Sec. II is required when the energy E falls below one or more of the threshold E_i. That procedure, namely, the treatment of configuration mixing by solving the Lippmann-Schwinger Eq. (11) followed by substitution of the Green's function expansion, remains valid—but only in principle—as long as E exceeds at least one threshold. Two practical difficulties arise which must be bypassed.

Firstly, when E drops below a channel threshold E_i, the energy parameter $\epsilon_i = E - E_i$ becomes negative. The δ function singularity in Eqs. (9) and (10) becomes then inoperative, except for isolated values of E at which ϵ_i coincides with one of the discrete negative levels ϵ_{in}. Thereby, the parameter C_i of that channel drops out, in accordance with the fact that the degeneracy of eigenstates equals the number of open channels (i.e., of channels with $E > E_i$). A real difficulty stems instead from the changed character of the $(\epsilon_i - \epsilon_{in})^{-1}$ singularity in Eqs. (10)–(12). The contribution of this singularity depends on ϵ_i smoothly only as long as the ϵ_{in} form a continuum and the principal part is taken in the $\sum_n$, but it oscillates sharply when the set of ϵ_{in} is discrete; indeed, the $\sum_n$ becomes very large whenever ϵ_i gets much closer to one particular level ϵ_{in} than to any other one. This singular behavior, familiar in the study of Green's functions of systems with discrete spectra (Ref. 6, p. 99), makes numerical treatment of Eq. (11) quite impractical and contributes to its solution singularities that reflect the presence of autoionizing levels in the closed channels with $E_i > E$. One might say that the discrete structure of the spectrum of ϵ_{in} renders inoperative the stipulation of principal part integration across the pole of $(\epsilon_i - \epsilon_{in})^{-1}$.

A second difficulty arises at energies E close to any of the thresholds E_i, owing to singularities of the continuum $f_{in}(r)$ as functions of ϵ_{in} at $\epsilon_{in} = 0$. This difficulty is particularly conspicuous in the absence of a Coulomb field, as $f_{in}(r)$ vanishes at the threshold for finite values of r, causing the matrix elements of V and K to vanish as well, with branch point singularities.

These difficulties are bypassed by the quantum-defect theory through the following approach. One remarks that both the discrete structure of the spectrum for negative ϵ_{in} and the singularities at $\epsilon_{in}=0$ result from boundary conditions imposed on the $f_{in}(r)$ at $r=\infty$. On the other hand the calculation of configuration mixing in terms of a K matrix, as formulated in Sec. II, deals exclusively with short-range interactions. Accordingly one should extrapolate freely the K-matrix calculation below any or all of the thresholds E_i by removing temporarily the boundary conditions at $r=\infty$ upon the eigenfunctions of the radial operators h_i. Thereby one will obtain a modified K matrix—to be called $K^{(s)}$—that depends smoothly on E. The discrete structure of spectra for negative ϵ_i will reemerge in a further step of calculation, when the boundary conditions at $r=\infty$ are imposed again.[3]

As anticipated in Sec. I, the results to be obtained in this manner, by taking into account the short-range interactions equally below any threshold as above it, will be substantially equivalent to those obtained by the R-matrix procedures which are manifestly independent of threshold effects and of boundary conditions at $r=\infty$.[4] In fact, the calculation of the $K^{(s)}$ matrix by solving the modified Lippmann-Schwinger equation, to be presented here, may be regarded as a configuration mixing technique for the solution of the core problem in R-matrix theory. This remark contributes to our goal of illustrating the connections between alternative theoretical approaches.

A. Radial functions for negative energy

The approach to be followed requires smooth, analytic if possible, extrapolation of continuum wave functions $f_i(\epsilon_i, r)$ into the range of negative ϵ_i. Seaton's MQDT (Ref. 2) and its extensive applications by his school also involve extrapolation of K matrices, or rather of equivalent R matrices, which are calculated numerically for $\epsilon_i>0$ but are also applied for negative values of ϵ_i. Here we introduce the concept of calculating the matrix $K_{ij}^{(s)}(E)$ independently for different values of E, larger or smaller than any of the threshold E_i.

Regarding the extrapolation of wave functions to negative energies, consider initially that construction of a regular solution $f_{in}(r)$ of Eq. (4), proceeding from $r=0$ to any finite r, develops in the same manner whether ϵ_{in} is positive or negative; indeed the zero point of ϵ_{in} is defined as the value of the potential in h_i at $r=\infty$, which is not relevant to the integration at lower r. Similarly, one can construct a second, independent solution of Eq. (4) at each ϵ_{in}. Our treatment in Sec. II requires, however, that we identify at each positive energy ϵ_i a *standard pair* of solutions of Eq. (4), normalized per unit energy, of which f_i is regular at $r=0$ and g_i lags in phase by 90° at large r. The extrapolation of this standard pair to negative values of ϵ_i—which need not coincide with eigenvalues ϵ_{in}—has been provided by Seaton[2] for Coulomb field functions. An extension of his results is discussed in a separate paper[9] and will only be outlined here.

At the outset, we can identify an alternative base pair of solutions of Eq. (4), $f_i^0(\epsilon_i, r)$ and $g_i^0(\epsilon_i, r)$, for any ϵ_i by imposing boundary conditions at $r=0$ rather than at large r. These conditions do not depend on ϵ_i and fix the Wronskian of the pair. This pair coincides with the standard pair of Sec. II at large r when $\epsilon_i=0$ and the field of $h_i(r)$ is Coulombic. Otherwise the base pair identified at $r=0$ is related to the standard pair identified for large r at $\epsilon_i>0$ by a unimodular (but not unitary) transformation which leaves the Wronskian invariant. Our procedure consists of *extrapolating this transformation* to negative ϵ_i; we thus generate a standard pair (f_i, g_i) normalized at large r, starting from the base pair identified at $r=0$ for any value of ϵ_i.[9] By "large r" we mean r values comparable to or larger than the core radius r_0. For negative ϵ_i, we shall also consider a third pair of base functions, obtained by orthogonal transformation of the standard pair,

$$\begin{aligned} u_i(\epsilon_i, r) &= f_i(\epsilon_i, r)\sin\chi_i - g_i(\epsilon_i, r)\cos\chi_i\,, \\ v_i(\epsilon_i, r) &= -f_i(\epsilon_i, r)\cos\chi_i - g_i(\epsilon_i, r)\sin\chi_i\,. \end{aligned} \tag{15}$$

This pair, and hence the angle $\chi_i(\epsilon_i)$, is identified by the requirement that $v_i(\epsilon_i, r)$ vanishes at $r=\infty$. The discrete eigenvalues $\epsilon_{in}<0$ of h_i are thus identified by the condition $\chi_i(\epsilon_{in})=n\pi$. (In the quantum-defect literature χ is indicated by $\pi\nu$ for Coulomb functions.) The functional relationship between the parameter χ_i and the energy ϵ_i also serves to represent the normalization ratio of a discrete wave function $f_{in}(r)$ to the standard function $f_i(\epsilon_{in}, r)$,

$$f_{in}(r) = N_{in} f_i(\epsilon_{in}, r)\,, \quad N_{in}^2 = \pi(d\epsilon_i/d\chi_i)_{\epsilon_{in}}\,. \tag{16}$$

[In Sec. II, i.e., for $\epsilon_{in}>0$, f_{in} was normalized per unit energy and hence identical to $f(\epsilon_{in}, r)$.]

B. Lippmann-Schwinger equation for negative energy

We return now to the problem of solving Eq. (6) for the coefficients D_{in} at energies E lower than the channel threshold E_i. Having removed temporarily the requirement that Ψ remain finite at $r=\infty$, we can allow Ψ to include the term represented by Eq. (9) even for $\epsilon_i<0$; later application of the boundary condition will restrict the coefficient C_i.[10] We might then represent D_{in} once again by Eq. (10), but an adjustment is required to make its pole term yield a smooth contribution in the discrete, i.e., to achieve the same effect as the principal part symbol does in the continuum. The adjustment consists of subtracting from D_{in} a term that just cancels its pole. Finally our notation must also be adjusted, because the $\sum_n$ does not generally include, for closed channels, a term with $\epsilon_{in}=\epsilon_i$. Thus we rewrite Eqs. (5) and (10) in a form that distinguishes the contributions of discrete and continuous spectra in terms of the step function $\Theta(x)$, which equals 1 for $x\geqslant 0$ and 0 for $x<0$,

$$\Psi=\sum_i\left(f_i(\epsilon_i,r)\Phi_i d_i+\sum_n f_{in}(r)\Phi_i D_{in}\right), \qquad (17)$$

$$d_i=C_i-\Theta(-\epsilon_i)\pi\cot\chi_i(\epsilon_i)\times\sum_k(f_i(\epsilon_i)\Phi_i|K^{(s)}|f_k(\epsilon_k)\Phi_k)C_k, \qquad (18)$$

$$D_{in}=[\Theta(\epsilon_i)P+\Theta(-\epsilon_i)](\epsilon_i-\epsilon_{in})^{-1}\times\sum_k(f_{in}\Phi_i|K^{(s)}|f_k(\epsilon_k)\Phi_k)C_k. \qquad (19)$$

To verify that the contributions of the poles of Eqs. (18) and (19) cancel out, consider that $\pi\cot\chi_i$ has poles $\pi[\chi_i(\epsilon_i)-\chi_i(\epsilon_{in})]^{-1}$ and that the normalization ratio of $f_i(\epsilon_i)$ and of f_{in} is given by Eq. (16).

Upon substitution of Eq. (17) in the Schrödinger equation $(H_0+V-E)\Psi=0$, the operator H_0-E yields zero when applied to the term with the coefficient d_i and yields $\epsilon_{in}-\epsilon_i$ for the terms with D_{in}. The analog of Eq. (11) results then by projecting the equation on $f_{in}\Phi_i$ and setting to zero the coefficient of each C_k,

$$\begin{aligned}(f_{in}\Phi_i|K^{(s)}(E)|f_k(\epsilon_k)\Phi_k)&=(f_{in}\Phi_i|V|f_k(\epsilon_k)\Phi_k)\\&+\sum_j\sum_m(f_{in}\Phi_i|V|f_{jm}\Phi_j)[\Theta(\epsilon_j)P+\Theta(-\epsilon_j)](\epsilon_j-\epsilon_{jm})^{-1}(f_{jm}\Phi_j|K^{(s)}(E)|f_k(\epsilon_k)\Phi_k)\\&-\sum_j(f_{in}\Phi_i|V|f_j(\epsilon_j)\Phi_j)\Theta(-\epsilon_j)\pi\cot\chi_j(\epsilon_j)(f_j(\epsilon_j)\Phi_j|K^{(s)}(E)|f_k(\epsilon_k)\Phi_k).\end{aligned} \qquad (20)$$

This equation differs from Eq. (11) mainly by the insertion of its last term, which effectively replaces the symbol P for negative values of ϵ_j. As contemplated above, this new term causes the $K^{(s)}$ matrix elements to remain smooth even for energies E corresponding to poles of $(\epsilon_j-\epsilon_{jm})^{-1}$ with negative values of ϵ_j. (The resonances observed experimentally at those energies will be represented instead by sharp variations of the coefficients C_j.)

Actual solution of Eq. (20) to yield rows of the $K^{(s)}$ matrix with negative values of ϵ_{in} extends the range of practical application of the Lippmann-Schwinger equations. It will actually be unnecessary to solve Eq. (20) for each of the infinitely numerous levels n of a Rydberg series. For negative values of ϵ_{in} one should rather divide Eq. (20) by the normalization coefficient N_n, and thereby replace the discrete wave function f_{in} in the row indices of $K^{(s)}$ by the corresponding continuum-normalized standard function $f_i(\epsilon_{in})$; solution of the equation for a rather coarse mesh of values of ϵ_{in} should prove adequate for negative as it does for positive values of ϵ_{in}. Similarly, evaluation of the $\sum_m$ over negative ϵ_{jm} may be simplified in Eq. (20) by factoring the normalization N_{jm} out of f_{jm} in the matrix elements, after which the matrix elements depend smoothly on ϵ_{jm} and the $\sum_m N_{jm}^2(\epsilon_j-\epsilon_{jm})^{-1}$ approximates $\pi\cot\chi_j(\epsilon_{jm})$.

C. Green's function for negative energy

We come thus eventually to reducing our wave function (17) to the form utilized by the quantum-defect theory. Here, as in Sec. II, the $\sum_n$ in Eq. (17) operates on the same set of n-dependent factors as the $\sum_n$ in Eq. (7) and can thus be replaced by an alternative expression of the Green's function $\mathcal{G}_i(\epsilon_i;r,r')$. However, for negative values of ϵ_i, the appropriate expression of $\mathcal{G}_i$ is no longer given by Eq. (8).

As discussed, e.g., on p. 99 of Ref. 6, the Green's function of an operator $h_i(r)$ has poles at the negative eigenvalues ϵ_{in} of its discrete spectrum. These poles are not represented by the simple expression $\pi g_i(\epsilon_i,r)f_i(\epsilon_i,r')$ on the right of Eq. (8). They are included by subtracting from that expression a term $f_i(\epsilon_i,r)f_i(\epsilon_i,r')$ with a suitable coefficient that diverges at $\epsilon_i=\epsilon_{in}$ and vanishes at or near the middle of the interval between two successive poles, ϵ_{in} and $\epsilon_{i,n+1}$;

comparison with Ref. 6 shows this coefficient to coincide with our function $\pi\cot\chi(\epsilon_i)$.

We conclude that the expression on the right of Eq. (8) remains indeed relevant for negative values of ϵ_i. It no longer serves to represent the contribution $\mathcal{G}_i(\epsilon_i; r, r')$ of the $\sum_n$ in Eq. (17), but the *combined contribution* of $\mathcal{G}_i$ and of the function $-f_i(\epsilon_i, r)\pi\cot\chi_i f_i(\epsilon_i, r')$ which arises from the term of Eq. (17) with the coefficient d_i. This expression might be indicated by $\mathcal{G}^{(s)}$ and described as a smoothed-out Green's function. Thereby Eq. (17) reduces, for $r > r_0$, to the final Eq. (14) of Sec. II. In other words, Eq. (14) *remains valid for negative values of* ϵ_i, provided we use the reaction matrix $K^{(s)}_{ij}(E)$ calculated from the singularity free Eq. (20).

D. Resonances and threshold effects

This result completes our derivation of the quantum-defect expression of a wave function outside the core from the configuration-mixing expression with coefficients determined by a Lippmann-Schwinger equation. As anticipated above, the discrete structures of spectra observed below detachment thresholds are introduced in quantum-defect treatments as a subsequent step, by enforcing the requirement that the radial functions in channels with negative ϵ_i remain finite at $r \to \infty$. This requirement is formulated by replacing in Eq. (14) the standard pair of functions (f_i, g_i) by the alternative base pair (u_i, v_i), defined by Eq. (15), and setting to zero the coefficient of the diverging function u_i. This procedure gives

$$\Theta(-\epsilon_i)\left(\sin\chi_i(\epsilon_i)C_i - \pi\cos\chi_i(\epsilon_i)\sum_j K^{(s)}_{ij}(E)C_j\right) = 0\,. \tag{21}$$

Resonant behavior of the coefficients C_j occurs at near-zero minima of the determinant

$$\mathrm{Det}|\Theta(-\epsilon_i)[\sin\chi_i\delta_{ij} - \pi\cos\chi_i K^{(s)}_{ij}]\Theta(-\epsilon_j)|\,. \tag{22}$$

When all channels are closed, the system of equations (21) has nonzero solutions C_j only when its determinant, Eq. (22) vanishes; this condition fixes the energy levels of the bound states of core + electron.

The additional singularities, which are associated with threshold behavior, at $\epsilon_i = 0$, particularly in the absence of long-range forces, are removed instead by an additional procedure with which we do not concern ourselves here. This procedure involves a further smoothing out of the Eq. (20), beyond the insertion of the $\cot\chi_i$ term and the replacement of the discrete radial functions f_{in} by the $f_i(\epsilon_i)$; it replaces the $f_i(\epsilon_i)$ of the standard pair with the base functions normalized at $r = 0$, through the unimodular transformation mentioned above. This transformation is carried out explicitly in Seaton's work[2]; it replaces the calculation of the $K^{(s)}$ matrix through Eq. (20) by the calculation of a still smoother, but substantially equivalent, R matrix.

ACKNOWLEDGMENTS

I am indebted to Christian Jungen and especially to Dan Dill for stimulating discussions and suggestions. I also thank M. Inokuti for reviewing the manuscript. This work was supported by the U. S. Energy Research and Development Administration, Division of Physical Research, Contract No. COO-1674-130.

---

[1] C. Jungen and O. Atabek, J. Chem. Phys. 16, 5584 (1977).

[2] M. J. Seaton, Proc. Phys. Soc. Lond. 88, 801 (1966).

[3] U. Fano, J. Opt. Soc. Am. 65, 979 (1975).

[4] P. G. Burke and D. Robb, Adv. Atomic and Mol. Phys. 11, 144 (1975); U. Fano and C. M. Lee, Phys. Rev. Lett. 31, 1573 (1973); C. M. Lee, Phys. Rev. A 10, 584 (1974); see also "R-Matrix Symposium" in *Invited Papers to the Tenth ICPEAC, Electronic and Atomic Collisions*, edited by G. Watel (North-Holland, Amsterdam, 1977).

[5] This formulation might be extended to include long range, but *local*, potentials that couple different channels (i, j), as outlined, e.g., by E. S. Chang and U. Fano, Phys. Rev. A 6, 173 (1972).

[6] See, e.g., L. S. Rodberg and R. M. Thaler, *The Quantum Theory of Scattering* (Academic, New York, 1967), Chap. 4, especially Sec. 3.

[7] See, e.g, Ref. 6, pp. 239–240.

[8] See, e.g., P. L. Altick and E. N. Moore, Phys. Rev. 147, 59 (1966); A. F. Starace, Phys. Rev. A 2, 118 (1970).

[9] C. Greene *et al*. (unpublished).

[10] The traditional application of configuration mixing would represent Ψ at large r by a superposition of the decaying exponentials of many different wave functions f_{in}. The MQDT procedure replaces this superposition by the single function $v_i(\epsilon_i, r)$ with the value of ϵ_i at which $\chi_i(\epsilon_i) = 0$.