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Phase-Amplitude Method in Atomic Physics. I. Basic Formulas for an Electron in an Ionic Potential*

J. L. Dehmer[†]

Departments of Chemistry and Physics, University of Chicago, Chicago, Illinois 60637

and

U. Fano

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

(Received 27 February 1970)

The radial Schrödinger equation for a modified Coulomb field is separated into two first-order equations for a "phase" function and an "amplitude" function which vary only in the non-Coulomb region $r < r_0$. At $r = r_0$, these functions are related to the mixing parameter and normalization constant of quantum-defect theory. Integrals over the range $[0, r_0]$ give the scattering phase shift and the wave function's amplitude near the nucleus. Phase shifts for negative energies serve to calculate the discrete eigenvalues of an atom or positive ion. A numerical procedure for this approach is outlined.

I. INTRODUCTION

This paper originates from an attempt to explain the behavior of inner-shell photoabsorption cross sections. Since these cross sections are proportional[1] to the square of the final state's amplitude near the nucleus, their interpretation requires a suitable formulation of this amplitude in terms of the factors that influence it. The phase-amplitude method[2] (PAM) serves this purpose by representing the inner amplitude in terms of a definite integral over the non-Coulomb part of the potential, provided one utilizes as basis functions a pair of solutions of the Coulomb-field wave equation. The same method also produces a finite-range integral expression for the exact scattering phase shift.

In the last decade, Calogero and others[3] have developed this method in the context of potential scattering. However, this recent progress has treated explicitly only potentials which vanish faster than r^{-1} and has not yet applied the PAM to the broader range of problems for which it is useful.

This paper further develops the PAM in three ways: (a) It derives basic PAM formulas for the case of a modified Coulomb field. (b) It describes

the connection between this approach and the quantum-defect theory (QDT). Specifically, the PAM provides the mixing parameter which is the basis for a QDT treatment of excited and ionized electrons, whereas QDT furnishes the normalization of the wave function at $r = r_0$ from which the PAM produces a description of penetrating orbits. (c) It provides a framework for the application of the PAM to several problems in atomic and molecular physics, some of which will be pursued in subsequent papers.

The present discussion is limited to local central potentials. The extension to nonlocal, complex, and many-body potentials is outlined by Calogero and others,[3] but its application will require further work.

II. PHASE-AMPLITUDE METHOD

Consider a single electron whose radial motion in a central field is described by a Schrödinger equation whose Hamiltonian $H(r)$ can be partitioned into two parts:

$$H(r)P(r) = [H_0(r) - U(r)]P(r) = EP(r). \tag{1}$$

This partition is chosen so that H_0 has a pair of known independent solutions (u_1, u_2), satisfying

$$H_0(r)u_i(r) = Eu_i(r), \quad i = 1, \ 2$$
$$u_1(0) = 0 \ . \tag{2}$$

The magnitude of $U(r)$ is *not* required to be small.
The PAM proceeds by the ansatz

$$P(r) = \alpha(r)\{u_1\cos[\delta(r)] - u_2\sin[\delta(r)]\}$$
$$= \alpha(r)\overline{P}(r) \tag{3}$$

and the constraint[4]

$$P'(r) = \alpha(r)\{u_1'\cos[\delta(r)] - u_2'\sin[\delta(r)]\}, \tag{4}$$

where primes denote differentiation with respect to r, and $\alpha(r)$ and $\delta(r)$ are the "amplitude" and "phase" functions, respectively. (3) and (4), together with the Schrödinger equation, serve to eliminate $P(r)$. Combining Eqs. (3) and (4), we get

$$\frac{\alpha'}{\alpha} = \delta' \, \frac{(u_1\sin\delta + u_2\cos\delta)}{(u_1\cos\delta - u_2\sin\delta)} \ . \tag{5}$$

Similarly, Eqs. (1) and (4) combine to give

$$\frac{\alpha'}{\alpha} = \frac{\delta'(u_1'\sin\delta + u_2'\cos\delta) - U(u_1\cos\delta - u_2\sin\delta)}{(u_1'\cos\delta - u_2'\sin\delta)}. \tag{6}$$

Subtracting Eq. (5) from Eq. (6) shows that δ is independent of α and gives differential forms for the equations which are solved in the application of the PAM:

$$\delta' = U(u_1\cos\delta - u_2\sin\delta)^2/W(u_1, u_2) \ , \tag{7}$$

$$\frac{\alpha'}{\alpha} = -\frac{U}{W(u_1, u_2)} \, (u_1\cos\delta - u_2\sin\delta)$$

$$\times (u_1\cos[\delta + \tfrac{1}{2}\pi] - u_2\sin[\delta + \tfrac{1}{2}\pi]) \ . \tag{8}$$

$W(u_1, u_2)$ indicates the Wronskian determinant of u_1 and u_2, which is nonzero if u_1 and u_2 are independent solutions of Eq. (2). The quantity squared in Eq. (7) is just $\overline{P}(r)$, the radial wave function stripped of its amplitude function. Equation (8) contains this same function multiplied by a similarly reduced wave function phase shifted by $\tfrac{1}{2}\pi$. This product behaves like $\sin 2\phi$, where ϕ is the phase of $\overline{P}$, so that the sign of α'/α changes with r, depending on the local sign of U and the quadrant of ϕ.

The appearance of U as a multiplier of the right-hand side of both Eqs. (7) and (8) suggests that H_0 should contain all long-range terms from the total potential. In this way, the phase and amplitude functions become constant at a finite distance r_0 from the nucleus so that Eqs. (7) and (8) have integral forms involving definite integrals

$$\delta(r) = W^{-1}\int_0^r U(u_1\cos\delta - u_2\sin\delta)^2 dr \ , \tag{7'}$$

$$\alpha(r) = \alpha(r_0)\exp[-W^{-1}\int_r^{r_0} U(u_1\cos\delta - u_2\sin\delta)$$

$$\times (u_1\sin\delta + u_2\cos\delta)dr] \ . \tag{8'}$$

In order that the wave function remain finite at the nucleus we have required $\delta(0) = 0$. Accordingly, one generates the phase function by starting at $r = 0$ and extending the range of integration in Eq. (7') to increasingly large values of r until r_0 is reached. Thereafter, U vanishes and δ remains constant; the value of $\delta(r_0)$ determines the asymptotic phase shift. Under the same circumstances, the constant $\alpha(r_0)$ in Eq. (8'), determined by normalization at $r = \infty$, depends only on $\delta(r_0)$ (see Sec. IV). Therefore, the amplitude function $\alpha(r)$ is obtained by a simple quadrature over the interval $[r, r_0]$, once the phase function is known. By including only short-range potentials in U, one also incorporates the familiar behavior of the standard long-range potentials into the basis set (u_1, u_2), while displaying explicitly in Eqs. (7') and (8') the effects of the low r potentials which distinguish one atom from another.

III. COULOMB FUNCTIONS

The main purpose of Sec. II requires a set of functions (u_1, u_2) which include the effects of all long-range potentials. We will assume that in the presence of a Coulomb tail, the asymptotic region is dominated by the Coulomb and centrifugal forces so that sufficient accuracy is achieved by truncat-

ing all other forces at some radius $r = r_0$. These other forces, such as polarization, could be included in H_0 by a modification of the QDT used below. For now, H_0 will be the Coulomb Hamiltonian

$$[H_0 - E]u_i = \left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2z}{r} - E\right)u_i = 0 , \quad (9)$$

where r is in a.u., E is in rydbergs, and l is the angular-momentum quantum number.

Two alternative sets of Coulomb functions are suited for construction of solutions in complementary regions of the (E, r) plane. The first set contains the independent Coulomb functions f and g described by Seaton.[5] Introducing the variables

$$\rho = zr ,$$

$$\epsilon = -1/\kappa^2 = E/z^2 ,$$

$$\kappa = \nu , \quad \text{for } \epsilon < 0 \quad (10)$$

$$= i\gamma, \quad \text{for } \epsilon > 0 ,$$

(f, g) are defined by the series expansions[6]

$$f(\kappa, l; \rho) = \frac{(2\rho)^{l+1}e^{-\rho/\kappa}}{\Gamma(l+1-\kappa)} \sum_{\sigma=0}^{\infty} \frac{\Gamma(l+1-\kappa+\sigma)}{\Gamma(2l+2+\sigma)\sigma!} \left(\frac{2\rho}{\kappa}\right)^{\sigma} , \quad (11)$$

$$g(\kappa, l; \rho) = \frac{A(\kappa, l)}{\pi} \ln(2\rho)f(\kappa, l; \rho) + \frac{(2\rho)^{-l}e^{-\rho/\kappa}}{\pi}$$

$$\times \sum_{\sigma=0}^{2l} \frac{(-1)^{\sigma+1}\Gamma(2l+1-\sigma)\Gamma(-l-\kappa+\sigma)}{\Gamma(-l-\kappa)\sigma!} \left(\frac{2\rho}{\kappa}\right)^{\sigma}$$

$$+ \frac{A(\kappa, l)(2\rho)^{l+1}e^{-\rho/\kappa}}{\pi\Gamma(l+1-\kappa)}$$

$$\times \sum_{\sigma=0}^{\infty} \frac{h_\sigma(\kappa, l)\Gamma(l+1-\kappa+\sigma)}{\Gamma(2l+2+\sigma)\sigma!} \left(\frac{2\rho}{\kappa}\right)^{\sigma} , \quad (12)$$

where

$$A(\kappa, l) = \prod_{p=0}^{l} (1 - p^2/\kappa^2) , \quad (13)$$

$$h_\sigma(\kappa, l) = [\psi(l+1-\kappa+\sigma) - \tfrac{1}{2}\psi(l+1-\kappa)$$

$$- \tfrac{1}{2}\psi(-l-\kappa) - \psi(2l+2+\sigma) - \psi(\sigma+1)] , \quad (14)$$

$$\psi(x) = \frac{d[\ln\Gamma(x)]}{dx} , \quad (15)$$

$$W(f, g) = 2z/\pi. \quad (16)$$

The Wronskian in Eq. (16) is evaluated by taking derivatives with respect to r.

The regular function f is related to more familiar confluent hypergeometric functions[7] by

$$f(\kappa, l; \rho) = \frac{(2\rho)^{l+1}e^{-\rho/\kappa}}{\Gamma(2l+2)} F(l+1-\kappa, 2l+2, 2\rho/\kappa)$$

$$= \frac{\kappa^{l+1}}{\Gamma(2l+2)} M_{\kappa, l+1/2}(2\rho/\kappa). \quad (17)$$

The important feature of (f, g) is their behavior at small ρ:

$$f(\kappa, l; \rho) = \left(\frac{1}{\Gamma(2l+2)}\right)(2\rho)^{l+1} - \left(\frac{1}{\Gamma(2l+3)1!}\right)(2\rho)^{l+2}$$

$$+ \left(\frac{1}{\Gamma(2l+4)2!} + \frac{(l+1)}{4\kappa^2\Gamma(2l+4)}\right)(2\rho)^{l+3} + 0(\rho^{l+4}) , \quad (18)$$

$$\pi g(\kappa, l; \rho) = A(\kappa, l) \ln(2\rho)f(\kappa, l; \rho)$$

$$- \Gamma(2l+1)(2\rho)^{-l} + \Theta + 0(\rho^{-l+3}) , \quad (19)$$

where

$$\Theta = \left[-\left(\frac{\varphi(1)}{1!}\right)(2\rho) + \left(\frac{\varphi(2)}{2!} - \frac{1}{8\kappa^2}\right)(2\rho)^2\right], \quad \text{for } l = 0$$

$$= \left[-\left(\frac{\Gamma(2l)}{1!}\right)(2\rho)^{-l+1} + \left(\frac{-\Gamma(2l-1)}{2!} + \frac{l\Gamma(2l-1)}{4\kappa^2}\right)\right.$$

$$\left. \times (2\rho)^{-l+2}\right], \quad \text{for } l \neq 0 \quad (20)$$

and $\varphi(x) = 1/x + 2\psi(x)$.

In both cases, κ^{-2} does not appear until the third term. This choice of normalization causes (f, g) to be energy independent as $\rho \to 0$. From Eq. (9), we see that this energy independence extends over the combined range $[-\bar{\epsilon} < \epsilon < \bar{\epsilon}, \rho \ll 2/\bar{\epsilon}]$ over which $\bar{\epsilon}$ is much smaller than the potential and kinetic energies. In addition (f, g) are entire analytic functions of energy.[5]

Since Eqs. (7) and (8) are solved in the interior of the atom, they are best cast in terms of (f, g). This makes the phase function δ and the logarithmic derivative α'/α energy independent in the region described above, and thereby confines the energy dependence of $P(r)$ as $r \to 0$ to the value of $\alpha(0)$.

Another set of functions $(\mathfrak{f}, \mathfrak{g})$ is useful for representing scattering states in the asymptotic region. For $\rho \gg 2/\epsilon > 0$,[8] these functions have the form

$$\mathfrak{f} \to (2\gamma/\pi)^{1/2}\sin(\omega) , \quad (21)$$

$$\mathfrak{g} \to -(2\gamma/\pi)^{1/2}\cos(\omega) , \quad (22)$$

where

$$\omega = \rho/\gamma - \tfrac{1}{2}l\pi + \gamma\ln(2\rho/\gamma) + \arg\Gamma(l+1-i\gamma) . \quad (23)$$

The pair of functions $(\mathfrak{f}, \mathfrak{g})$ is obtained by a linear transformation on (f, g):

$$\mathfrak{f}(\kappa, l; \rho) = B(\kappa, l)^{1/2} f(\kappa, l; \rho) \quad (24)$$

and

$$\mathcal{B}(\kappa,l;\rho) = B(\kappa,l)^{-1/2}[g(\kappa,l;\rho) + \mathcal{G}(\kappa,l)f(\kappa,l;\rho)] ,\quad(25)$$

where

$$B(\kappa,l) = A(\kappa,l)[1 - \exp(-2\pi\gamma)\,\mathrm{St}(\epsilon)]^{-1} ,\quad(26)$$

$$\mathcal{G}(\kappa,l) = \frac{A(\kappa,l)}{2\pi}\,\mathrm{Re}[\psi(l+1+\kappa) + \psi(-l+\kappa) - 2\ln(\kappa)] .$$

$$(27)$$

At $\epsilon = 0$, the two pairs of functions coincide because $B = 1$ and $\mathcal{G} = 0$.

IV. CONNECTION WITH QDT.

In accordance with QDT, we write the normalized wave function in the external Coulomb region as a linear combination of (f,g),

$$P(r) = N(\kappa,l)\{f(zr)\cos[\pi\xi(\kappa,l)]$$
$$- g(zr)\sin[\pi\xi(\kappa,l)]\} ,\quad \text{for } r \geq r_0 ,\quad(28)$$

where we have deleted the arguments κ and l from the Coulomb function symbols. In this expression, $\pi\xi$ is a modified phase shift related to Seaton's mixing parameters $\beta(\kappa,l)$ and $\eta(\kappa,l)$[5] and to the scattering phase shift $\delta_\infty(\kappa,l)$ by

$$\beta(\kappa,l) = \tan(\pi\xi),\quad(29)$$

$$\cot[\pi\eta(\kappa,l)] = \cot(\pi\xi) + \mathcal{G} ,\quad(30)$$

$$\cot[\delta_\infty(\kappa,l)] = \cot[\pi\mu(\kappa,l)] = B^{-1}[\cot(\pi\xi) + \mathcal{G}] .\quad(31)$$

Equation (31) introduces a function $\mu(\kappa,l)$ which is defined for all energies and coincides with the quantum defect for levels of the discrete spectrum. The function $\mu(\kappa,l)$ also replaces $\xi(\kappa,l)$ when (28) is replaced by the corresponding expression in terms of the basis set $(\mathfrak{f},\mathfrak{g})$,

$$P(r) = \mathfrak{N}(\kappa,l)\{\mathfrak{f}(zr)\cos[\pi\mu(\kappa,l)]$$
$$- \mathfrak{g}(zr)\sin[\pi\mu(\kappa,l)]\} .\quad(28')$$

When P is normalized, so that

$$\int_0^\infty P(\epsilon,l;r)P(\epsilon',l;r)\,dr = \delta(\epsilon - \epsilon') ,\quad(32)$$

the normalization constants of (28) are given by

$$N(\kappa,l) = (\tfrac{1}{2}z)^{1/2}B^{-1/2}\left(\frac{\sin\pi\mu}{\sin\pi\xi}\right)\theta^{-1/2}$$

$$= \frac{(\tfrac{1}{2}z)^{1/2}B^{1/2}}{\sin\pi\xi}[(\cot\pi\xi + \mathcal{G})^2 + B^2]^{-1/2}\theta^{-1/2},\quad(33a)$$

$$\mathfrak{N}(\kappa,l) = (\tfrac{1}{2}z)^{1/2}\theta^{-1/2} ,\quad(33b)$$

where

$$\theta = 1,\quad \text{for } \epsilon > 0$$

$$= \tfrac{1}{2}\nu_n^3 + \left(\frac{\partial\mu}{\partial\epsilon}\right)_{\epsilon=\epsilon_n} ,\quad \text{for } \epsilon < 0.\quad(34)$$

Since, for $\epsilon < 0$, θ is only required at discrete eigenvalues, we use the subscript n to denote the principal quantum number of a discrete state. The nature of the quantity θ is discussed elsewhere.[9]

Comparison of Eqs. (3) and (28) provides the connection between $\delta(r_0)$ and $\alpha(r_0)$ and the parameters from QDT. The exact values of the PAM parameters depend on the choice of Coulomb functions used in Eq. (3) and are expressed for the alternative sets defined in Sec. III by

$$\delta(r_0) = \pi\xi,\quad \text{for } (f,g)\quad(35a)$$

$$= \pi\mu,\quad \text{for } (\mathfrak{f},\mathfrak{g}),\quad(35b)$$

and $\quad \alpha(r_0) = N,\quad \text{for } (f,g)\quad(36a)$

$$= \mathfrak{N},\quad \text{for } (\mathfrak{f},\mathfrak{g}) .\quad(36b)$$

Using Eqs. (16) and (35a) in Eq. (7'), we obtain

$$\xi = \frac{1}{2z}\int_0^{r_0} U(r)[f(zr)\cos\delta(r)$$
$$- g(zr)\sin\delta(r)]^2\,dr.\quad(37)$$

This result from the PAM permits application of QDT to atoms throughout the periodic table with model potentials of the form $U(r) + 2z/r$ without resorting to use of experimental data. The phase shift ξ also determines the value of the normalization constant N so that the second PAM equation may now be solved using the boundary condition expressed in Eq. (36a), whereby Eq. (8') becomes

$$\alpha(r) = N\exp\left\{-\frac{\pi}{2z}\int_r^{r_0} U(r)[f(zr)\cos\delta(r)\right.$$
$$- g(zr)\sin\delta(r)][f(zr)\sin\delta(r)$$
$$\left.+ g(zr)\cos\delta(r)]\,dr\right\} .\quad(38)$$

Since for atomic systems $U \geq 0$, we see from Eq. (7') that $\delta(r)$ will be a monotonic function of r. Therefore, the relative energy dependence of the phase shifts $\pi\xi$ and $\pi\mu$ reflect the relative energy dependence of their respective phase functions. An example of the energy dependence of $\pi\xi$ and $\pi\mu$ is shown in Fig. 1. The phase shifts are calculated for the $l = 1$ channel of atomic sulfur using a Hartree-Fock-Slater potential[10] which becomes pure Coulomb at $r_0 \sim 3$. The function $\pi\eta$ is included for comparison. Note that for $\epsilon < \tfrac{1}{2}$, $\pi\xi$ is more slowly varying than $\pi\mu$, whereas, for $\epsilon > 1$, $\pi\mu$ varies more slowly. This remark illustrates the value of introducing two alternative sets of Coulomb functions in connection with modified Coulomb potentials. Note that μ, ξ and η coincide,
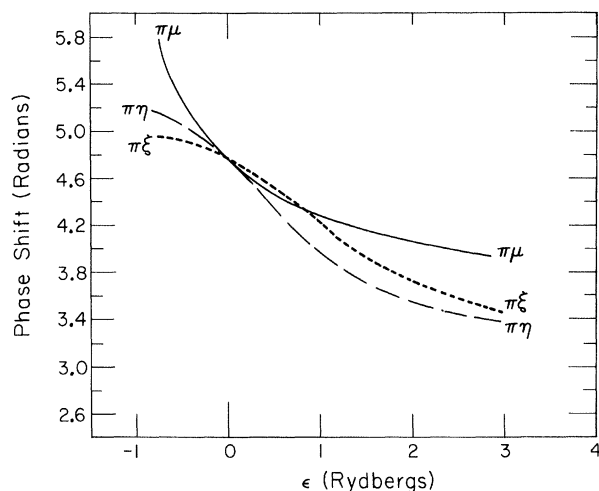
FIG. 1. $\pi\xi$, $\pi\mu$, and $\pi\eta$ phase shifts for the $l=1$ channel of atomic sulfur represented by a Hartree-Fock-Slater potential.

like the function pairs, at $\epsilon = 0$.

V. DISCUSSION

In problems of potential scattering, the important quantity is the scattering phase shift $\delta_\infty = \pi\mu$. When the phase function is calculated using (f,g) as basis functions, the phase shift δ_∞ is obtained by substituting Eq. (37) into Eq. (31). Note that this procedure avoids any explicit calculation of the normalized wave function. Furthermore, a plot of the integrand of Eq. (37) as a function of r displays the contribution to the phase shift from different parts of the potential.[11] This approach can show, for example, what regions of space produce the rapid phase increase by π near a shape resonance. Note also that for $\delta \ll 1$, $\cos\delta \sim 1$ and $\sin\delta \sim 0$ so that Eq. (37) reduces to the first Coulomb-Born approximation for the phase shift.

The cross section for photoabsorption is proportional to the square of the dipole matrix element $R(\epsilon l, \epsilon' l')$:

$$R(\epsilon l, \epsilon' l') = \int_0^\infty r P_{\epsilon l}(r) P_{\epsilon' l'}(r) dr$$

$$= \int_0^\infty r P_{\epsilon l}(r) \alpha(r) \overline{P}_{\epsilon' l'}(r) dr .\qquad (39)$$

Mechanistically, one may distinguish two stages of the photoabsorption process. The first one is the photoabsorption "proper" during which the photon's energy is transferred to the electron occupying $P_{\epsilon l}$. This takes place in the region of space occupied by $P_{\epsilon l}$ and is followed by the "escape" of the excited electron from this region. For inner shell processes, the language of PAM serves to factor Eq. (39) in a way which roughly corresponds

to these two stages

$$R(\epsilon l, \epsilon' l') = \{N \exp[\int_0^r 0 - (\alpha'/\alpha) dr']\} ,$$

$$\{\int_0^\infty r P_{\epsilon l}(r) \exp[\int_0^r (\alpha'/\alpha) dr'] \overline{P}_{\epsilon' l'}(r) dr\}$$
(40)

$$= \alpha(0)\overline{R}(\epsilon l, \epsilon' l') ,$$

where $\alpha(0)$ and $\overline{R}$ represent the two braces, respectively. The reduced matrix element $\overline{R}$ corresponds to the process in which an electron is excited from the initial state to a state normalized to unit amplitude at the nucleus. This standard normalization makes $\overline{R}$ independent of the behavior of U beyond the region occupied by $P_{\epsilon l}$. To form the actual matrix element R, one multiplies $\overline{R}$ by $\alpha(0)$, the amplitude of the final state at the nucleus. It is $\alpha(0)$ which depends on $\overline{P}$ and U in the outermost regions of the atom and, therefore, corresponds to the probability of escape. This correspondence is imperfect however, since $\alpha(0)$ pertains to an escape all the way from the nucleus rather than from the initial subshell $P_{\epsilon l}$.

For inner shell photoabsorption, the absorption proper occurs in a region of high potential and kinetic energies so that $\overline{R}$ is virtually independent of ϵ over tens to hundreds of eV, thus, confining the energy dependence to the factor $\alpha(0)$. This is illustrated in the case of K-shell absorption by combining a variation of ϵ, $\Delta\epsilon$, with U, i.e., by replacing U with

$$U' = U(1 \pm \Delta E/U). \qquad (41)$$

In the K shell, U is of the order of Z^2 so that $\overline{P}$ and α'/α will be insensitive to energy changes of $\Delta\epsilon \ll Z^2$. Therefore, the energy dependence of R will result from the contribution to $\alpha(0)$ from the range of integration outside the K shell.

The quantities $\alpha(0)$ and $\overline{R}$ in Eq. (40) are precise forms of the factors $N_{n'l'}$ and $\overline{R}$ described qualitatively in Ref. 1. Their mathematical formulation has been developed here as a preliminary step to explain the inner shell spectra of the sulfur atom in molecular SF_6. Since the absorption proper occurs deep in the central sulfur atom, the outstanding nonhydrogenic behavior observed[12] is due to the influence of the molecular field on the outgoing wave and can, therefore, be represented by $\alpha(0)$.

Equation (38) should also be useful for calculating the probability density of valence electrons in the inner part of atoms, e.g., in connection with hfs problems. Such calculations have been performed in the past by means of the Fermi-Segré formula[13] which utilizes a WKB approximation. However, it has not been readily clear to us how (38) does in fact reduce to this formula.

When $\epsilon < 0$, wave functions must vanish for $r \to \infty$. In the language of QDT, this condition is satisfied at energies for which

$$\mu(\epsilon,l) + \nu(\epsilon) = n, \quad n = l+1, l+2, \cdots , \tag{42}$$

where $\mu(\epsilon, l)$ is defined in Eq. (31), ν by Eq. (10) and n is the principal quantum number of the discrete state. If the left-hand side of Eq. (42) is plotted against energy, its intersection with an integer value n of the ordinate corresponds to the energy eigenvalue of the nth discrete state for the potential

$$V(r) = l(l+1)/r^2 - 2z/r - U(r) . \tag{43}$$

Regarding the numerical treatment of Eq. (37), it is easy to show, using the low r form of U,

$$U = 2(Z - z)/r, \quad r \to 0, \tag{44}$$

that $\quad \delta(r) = \left(\dfrac{\pi(Z-z)}{z\,\Gamma(2l+2)\Gamma(2l+3)} \right) (2zr)^{2l+2}$

$$+ \left(\frac{\pi(Z-z)}{z\,\Gamma(2l+2)\Gamma(2l+4)} \right)\left(-2 + \frac{2(Z-z)}{z(2l+1)} \right)$$

$$\times (2zr)^{2l+3} + \cdots . \tag{45}$$

This expansion serves to start the integration of Eq. (37). The fact that U is usually positive or zero everywhere for atomic systems means that δ will increase monotonically. Therefore, it may be calculated for increasing r by numerical integration of Eq. (7') utilizing a coarser mesh than is required for an oscillating radial wave function. Calogero and Ravenhall[14] demonstrated this feature by using both the PAM and the wave function approach to calculate phase shifts for s waves scattered by an attractive exponential potential. For all energies used, the PAM was more accurate and much less sensitive to the numerical mesh. Finally, let us point out that Eq. (37) may be evaluated using the expansions in Eqs. (11) and (12) of (f,g), since these expansions converge rapidly in the range $r < 5$ which encompasses the non-Coulomb part of most atoms in the approximation of Ref. 10.

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