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Theory of J-matrix Green's functions with applications to atomic polarizability and phase-shift error bounds

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The recently introduced Jacobi or J-matrix techniques for quantum scattering are developed to include the construction of exact analytic matrix elements of regular and Coulomb partial-wave zeroth-order and full Green's functions. Very simple results obtain for the unperturbed Green's functions, while full Green's functions require a single diagonalization of an $N \times N$ Hamiltonian matrix, where N is the number of basis functions coupled by the matrix truncated potential. In an application of the J-matrix Green's functions to the theory of atomic dynamic polarizabilities, the analytic result for hydrogen is derived, and it is shown how more general systems may be treated in a way which is superior to the usual N-term variational approach. In an application to error bounds for phase shifts, we show how the full Green's functions can be used to demonstrate the absence of false pseudoresonances in J-matrix scattering calculations, and bound the possible errors in computed phase shifts.

I. INTRODUCTION

The J-matrix technique was introduced recently as a natural and analytic approach to quantum scattering theory using infinite sets of L^2 Slater-type basis functions for the projectile wave function.[1,2] The original s-wave theory[1,2] has been generalized to all partial waves and to oscillator-type basis functions,[3] making the approach complete, viable, and well suited for electron-atom and nuclear collisions. Reference 3 also contains results for the partial-wave Coulomb case using Laguerre (Slater)-type basis sets. The goal of these papers has been the construction of exact scattering wave functions for well-defined model Hamiltonians which approximate physical Hamiltonians to arbitrary accuracy. This has been accomplished through the ability of the J-matrix techniques to account for the continuum solution of the unperturbed Hamiltonian without any approximation even though a discrete L^2 basis set is employed. The coupling potential is the only quantity approximated in the theory. It is truncated and represented as an $N\times N$ matrix V^N in the basis set. The infinite matrix problem $(H_0 - E + V^N)\psi \equiv (J + V^N)\psi = 0$ is solved exactly, yielding the desired wave functions. J is an infinite tridiagonal Jacobi matrix.

In this paper we focus attention on Green's functions rather than wave functions. The two are, of course, closely related. Basically, we wish to learn how to *invert* the infinite matrix $(J + V^N)$, i.e., we seek $G^N \equiv (J + V^N)^{-1}$. Whereas the Green's function is not required in practice in order to construct wave functions, it does serve several other useful purposes. We focus attention here on two applications, namely atomic dynamical polarizabilities and error bounds for J-matrix phase shifts.

Phase-shift error bounds,[4-10] and, in particular, the problem of false pseudoresonances,[5-10] have played an important role in the theory and application of algebraic variational methods in quantum scattering since Schwartz's discovery of the false-resonance problem in 1961.[6] While several methods are available to circumvent the difficulty in algebraic variational schemes, the pseudoresonances can still cause problems in applications of these algebraic methods.

The J-matrix methods differ from the algebraic variational theories[11] in that the operator inducing the continuous scattering spectrum, namely H^0, is treated exactly rather than by the *ad hoc* addition of continuumlike basis functions to an L^2 basis set. A J-matrix pseudoresonance would appear less likely since the Hamiltonian which is solved approximates the exact Hamiltonian in a well-defined and uniform way. In Sec. V it is shown that, provided a certain error estimator is less than unity, false resonances cannot occur (nor can real ones be missed!). The error can always be made small by enlarging the basis set used to describe V^N.

Another application of the Green's functions, to atomic polarizability, reveals that with the aid of the Coulomb J-matrix wave-function results,[3] we can obtain dynamic polarizabilities which contain, for example, complete Rydberg series of singularities characteristic of electron + core systems such as the alkali metals. In contrast to the variational results, which yield N pseudopoles for N input basis functions, the J-matrix approach provides the correct quantum-defect behavior. This is because the Coulomb H^0 part of the problem is treated analytically. This is discussed in Sec. IV where some analytic formulas for hydrogen, derived via J-matrix theory, are also presented.

For completeness we review briefly the results of previous work[1-3] in Sec. II. Section III shows how to construct zeroth-order and full J-matrix Green's functions. The analysis and practical effort is about the same as for the construction of wave functions.

II. REVIEW OF J-MATRIX THEORY FOR WAVE FUNCTIONS

In this section we briefly review the developments of Refs. 1–3 which are mainly concerned with the construction of wave functions, from which scattering information can be obtained. The key to the procedure lies in a choice of an unperturbed Hamiltonian H^0 which has a tridiagonal (Jacobi) matrix representation in an appropriate complete L^2 Laguerre (Slater), or oscillator basis set. The original s-wave theory[1,2] for Laguerre basis sets has received generalization[3] to all partial waves and to H^0's with Coulomb tails.

The unperturbed Hamiltonians, which so far have yielded soluble J-matrix forms, are

$$H_l^0 = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + \frac{Z}{r} \tag{2.1}$$

for the Laguerre-type basis set

$$\phi_n(\lambda r) = (\lambda r)^{l+1}\exp(-\tfrac{1}{2}\lambda r)L_n^{2l+1}(\lambda r) , \tag{2.2}$$

and

$$H_l^0 = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} \tag{2.3}$$

for

$$\phi_n(\lambda r) = (\lambda r)^{l+1}\exp(-\tfrac{1}{2}\lambda^2 r^2)L_n^{l+1/2}(\lambda^2 r^2) \tag{2.4}$$

which is an oscillator basis. Writing

$$\tilde{S}(r) = \sum_{n=0}^{\infty} s_n\phi_n , \tag{2.5a}$$

$$\tilde{C}(r) = \sum_{n=0}^{\infty} c_n\phi_n , \tag{2.5b}$$

it is possible to solve the equations

$$\langle\phi_m|H_l^0 - \tfrac{1}{2}k^2|\tilde{S}\rangle = 0, \quad m = 0, 1, \ldots, \infty \tag{2.6a}$$

$$\langle\phi_0|H_l^0 - \tfrac{1}{2}k^2|\tilde{C}\rangle = \beta \neq 0 , \tag{2.6b}$$

$$\langle\phi_m|H_l^0 - \tfrac{1}{2}k^2|\tilde{C}\rangle = 0, \quad m = 1, 2, \ldots, \infty \tag{2.6c}$$

subject to the boundary conditions (in the non-Coulomb case)

$$\tilde{S}(r) \xrightarrow[r\to\infty]{} \sin(kr - \tfrac{1}{2}l\pi) , \tag{2.7a}$$

$$\tilde{C}(r) \xrightarrow[r\to\infty]{} \cos(kr - \tfrac{1}{2}l\pi) . \tag{2.7b}$$

In the partial-wave Coulomb case we have[3]

$$\tilde{S}(r) \to \sin[kr + t\ln(2kr) - \tfrac{1}{2}l\pi + \sigma_l] , \tag{2.8a}$$

$$\tilde{C}(r) \to \cos[kr + t\ln(2kr) - \tfrac{1}{2}l\pi + \sigma_l] , \tag{2.8b}$$

where σ_l is a Coulomb phase shift.[12]

Equations (2.6), together with (2.5), are equivalent to the infinite-matrix problem

$$J \cdot s = 0 \tag{2.9a}$$

and

$$J \cdot c = \beta , \tag{2.9b}$$

where $J_{nm} = \langle\phi_n|H_l^0 - \frac{1}{2}k^2|\phi_m\rangle$ and where $\beta_n = \beta\delta_{n0}$. Since $J_{nm} \equiv 0$ if $|n - m| > 1$, it is easy to see that Eqs. (2.9) are three-term recursion relations for the coefficients s_n and c_n. These second-order difference equations in the variable (n) are completely analogous to the corresponding second-order differential equation in the variable (r). Both have two linearly independent solutions. Certain well-known special functions are identified as obeying the same recursion relations generated by the matrix J. The coefficients s_n and c_n are necessarily given in terms of these special functions. To finally pin down the coefficients s_n and c_n it is essential to choose the proper linear combination of the two independent special function recursion solutions in order to assure that the boundary conditions (2.7) or (2.8) are satisfied. The value of β in Eq. (2.6b) and Eq. (2.9b) is fixed by Eq. (2.7b). The reader is directed to Ref. 3 for a more complete discussion of the detailed H^0 solutions in the general case.

Here we shall quote some results which are useful for the sections to follow.

Case I: Laguerre basis set, $H_l^0 = -\frac{1}{2}d^2/dr^2 + l(l+1)/2r^2$:

$$s_n(\theta) = \frac{2^l\,\Gamma(l+1)n!}{\Gamma(n+2l+2)}(\sin\theta)^{l+1}C_n^{l+1}(\cos\theta) , \tag{2.10a}$$

$$c_n(\theta) = \frac{-2^l\Gamma(l+\frac{1}{2})n!}{\sqrt{\pi}\,\Gamma(n+2l+2)}\frac{1}{(\sin\theta)^l} \times {}_2F_1(-n-2l-1, n+1; \tfrac{1}{2}-l; \sin^2\tfrac{1}{2}\theta), \tag{2.10b}$$

where

$$\cos\theta = \frac{k^2/\lambda^2 - \frac{1}{4}}{k^2/\lambda^2 + \frac{1}{4}} ,$$

$C_n^{l+1}(\cos\theta)$ is a Gegenbauer polynomial,[13] and ${}_2F_1(-n-2l-1, n+1; \frac{1}{2}-l; \sin^2\frac{1}{2}\theta)$ is a hypergeometric function[14a] which is a finite polynomial in $\sin^2\frac{1}{2}\theta$.

Case II: Laguerre basis set, $H_l^0 = -\frac{1}{2}d^2/dr^2$

$+l(l+1)/2r^2+Z/r$ (Coulomb Case):

$$s_n(\theta)=2^l n!\,|\Gamma(l+1-it)|\,e^{(\pi/2+\epsilon\pi)t}e^{\theta t}\times(\sin\theta)^{l+1}P_n^{l+1}(\cos\theta;2Z/\lambda;-2Z/\lambda)\,, \tag{2.11a}$$

$$s_n(\theta)+ic_n(\theta)=\frac{-n!\,e^{i\sigma_l}e^{\pi t/2}e^{-\theta t}e^{-i(n+1)\theta}}{\Gamma(n+l+2-it)2^l(\sin\theta)^l}\times{}_2F_1(-l-it,n+1;n+l+2-it;e^{-2i\theta}), \tag{2.11b}$$

where

$$\epsilon=\begin{cases}(-1) & \text{for}\quad \theta[0,\pi]\\ (+1) & \text{for}\quad \theta[0,-\pi]\end{cases}$$

and $P_n^\lambda(Z;a;b)$ is a Pollaczek polynomial.[3,14b]

Case III: Oscillator basis, $H_l^0=-\frac{1}{2}d^2/dr^2+l(l+1)/2r^2$:

$$s_n(\eta^2)=\frac{(-1)^n n!\sqrt{2\pi}}{\Gamma(n+l+\frac{3}{2})}\exp(-\eta^2/2)\eta^{l+1}L_n^{l+1/2}(\eta^2)\,, \tag{2.12a}$$

$$c_n(\eta^2)=\left(\frac{2}{\pi}\right)^{1/2}\frac{\Gamma(l+\frac{1}{2})(-1)^n n!}{\Gamma(n+l+\frac{3}{2})}\exp(-\eta^2/2)\eta^{-l}\times{}_1F_1(-n-l-\tfrac{1}{2},\tfrac{1}{2}-l,\eta^2)\,, \tag{2.12b}$$

where $\eta=k/\lambda$.

With these solutions in hand, one can *approximate* the wave function ψ in

$$(H_l^0+V-\tfrac{1}{2}k^2)\psi=0 \tag{2.13}$$

by finding the *exact* solution to

$$(H_l^0+V^N-\tfrac{1}{2}k^2)\psi^N=0\,, \tag{2.14}$$

where

$$V^N=\sum_{n,n'=0}^{N-1}|\overline{\phi}_n\rangle\langle\phi_n|V|\phi_{n'}\rangle\langle\overline{\phi}_{n'}|$$

and $\overline{\phi}_n$ is the orthogonal complement of ϕ_n, i.e., $\langle\overline{\phi}_{n'}|\phi_n\rangle=\langle\phi_{n'}|\overline{\phi}_n\rangle=\delta_{nn'}$.[15] The exact solution of Eq. (2.14) is obtained by writing

$$\psi^N=\Phi+S(r)+tC(r)\,,$$

where

$$\Phi=\sum_{n=0}^{N-1}a_n\phi_n\,,\quad S(r)=\sum_{n=N}^{\infty}s_n\phi_n\,,\quad C(r)=\sum_{n=N}^{\infty}c_n\phi_n\,. \tag{2.15}$$

It then turns out that Eq. (2.14) can be satisfied in terms of $(N+1)$ linear algebraic equations involving the $(N+1)$ unknowns $\{a_n,t\}$.[1,3]

The method is simple to execute in practice. The various polynomials and hypergeometric functions are easily generated via the J-matrix recursion relation after the starting values have been given. The equation can be arranged so that a single diagonalization of $(H_l^0+V^N)_{N\times N}$ serves to specify the exact results at all energies in terms of a few simple quantities.[1,3]

From here, one can build in several directions. Multichannel scattering,[1-3] the problem of exchange,[2] and variational correction[1,2] of the results have previously been considered. Finding the Green's functions for the J-matrix equation represents yet another direction which we now pursue.

III. J-MATRIX GREEN'S FUNCTIONS

We shall deal first with the unperturbed partial-wave Green's function. In coordinate space, these satisfy the equation

$$(H_l^0-\tfrac{1}{2}k^2)G_l^0(r,r';k)=\delta(r-r')\,, \tag{3.1}$$

where H_l^0 is of the form (2.1) or (2.3). The solution of this equation is given in terms of the regular $S(r)$ and irregular $C(r)$ (sinelike and cosinelike) solutions of the corresponding homogeneous equation. Specifically, we have, for the outgoing Green's function,

$$G_l^{0(+)}(r,r';R)=-\frac{2S(r_<)[C(r_>)+iS(r_>)]}{W(S(r),C(r))}\,, \tag{3.2}$$

where $W(S,C)$ is the Wronskian of the regular and irregular solutions, which is independent of r.

The J-matrix analog of Eq. (3.1) is obtained by putting (3.1) in the appropriate L^2 basis set. This yields simply

$$\sum_{n''}\langle\phi_{n'}|H_l^0-\tfrac{1}{2}k^2|\phi_{n''}\rangle\langle\overline{\phi}_{n''}|G_l^{0(+)}|\overline{\phi}_n\rangle=\langle\phi_{n'}|\overline{\phi}_n\rangle=\delta_{n'n}\,,\qquad n,n'=0,1,\ldots,\infty\,, \tag{3.3a}$$

or, more compactly,

$$\sum_{n''}J_{n'n''}G_l^{0(+)}(n'',n;k)=\delta_{n'n}\,. \tag{3.3b}$$

Clearly,

$$G_l^{0(+)}(n'',n;k)=\langle\overline{\phi}_{n''}|(J^{(+)})^{-1}|\overline{\phi}_n\rangle\equiv[(J^{(+)})]_{n''n}\,, \tag{3.4}$$

so our burden is to invert the infinite tridiagonal matrix J, with attention given to the proper boundary condition (i.e., incoming, outgoing, or principal-value Green's function). Note the juxtaposition of basis functions and their orthogonal complements in Eq. (3.3a). This arrangement is important in the Laguerre case, since we have[15]

$$\phi_n(\lambda r)\equiv(\lambda r)^{l+1}\exp(-\tfrac{1}{2}\lambda r)L_n^{(2l+1)}(\lambda r)\,, \tag{3.5a}$$

$$\overline{\phi}_n(\lambda r) \equiv (\lambda r)^l \exp(-\tfrac{1}{2}\lambda r) L_n^{(2l+1)}(\lambda r) \times [\lambda n!/\Gamma(2l+n+2)]. \qquad (3.5b)$$

The J matrix is evaluated entirely in the ϕ_n basis, which is *not* orthogonal, but possesses a tridiagonal overlap matrix. This was the case in Refs. 1–3 also.

The easiest equation to work with is (3.3b), which is very similar to the wave function case, differing in the inhomogeneous term. In direct analogy with the coordinate space Green's function, Eq. (3.2), we suspect that the regular and irregular solutions (S and C, respectively) can be used to construct $G_l^{0(+)}(n,n';k)$, using a "greater than, less than" switching prescription to create a $\delta_{nn'}$ term on the right-hand side. Let us try

$$G_l^{0(+)}(n,n';k) = \alpha(k) s_{n_<}(c_{n_>} + i s_{n_>}) , \qquad (3.6)$$

where $\alpha(k)$ is to be determined and where s_n and c_n are given by the appropriate expression (depending on H_l^0 and the basis set) found in Eqs. (2.10)–(2.12). Finally, $n_<$ is the lesser of n and n', and $n_>$ the greater of the two.

Fixing n' and examining

$$\sum_{n''=0}^{\infty} J_{nn''} G_l^{0(+)}(n'',n';k) = \alpha(k) \sum_{n''=0}^{\infty} J_{nn''} s_{n_<}(c_{n_>} + i s_{n_>}), \qquad (3.7)$$

we can see that if $n \leqslant n'-1$ or $n \geqslant n'+1$, Eq. (3.7) gives zero. This follows from the tridiagonality of J and the fact that the s_n's and c_n's obey the corresponding three-term recursion relation. This leaves the $n=n'$ case, which is

$$\alpha(k)[J_{n',n'-1} s_{n'-1}(c_{n'} + i s_{n'}) + J_{n'n'} s_{n'}(c_{n'} + i s_{n'}) + J_{n',n'+1} s_{n'}(c_{n'+1} + i s_{n'+1})] = 1 , \qquad (3.8)$$

where we want to choose $\alpha(k)$ so that the inhomogeneity is unity, as indicated. Using the recursion relation, we can rewrite Eq. (3.8) as

$$\begin{aligned}\alpha(k) J_{n',n'-1}[s_{n'-1}(c_{n'} + i s_{n'}) - s_{n'}(c_{n'-1} + i s_{n'-1})] &= \alpha(k) J_{n',n'-1}[s_{n'-1}c_{n'} - s_{n'}c_{n'-1}] \\ &= 1 . \end{aligned} \qquad (3.9)$$

Again, using the recursion relation, we have

$$\alpha(k) J_{n'-2,n'-1}[-s_{n'-1}c_{n'-2} + s_{n'-2}c_{n'-1}] = 1 , \qquad (3.10)$$

and successive application yields

$$\alpha(k)[s_0\beta] = 1 , \qquad (3.11)$$

where we have used Eq. (2.6b), i.e.,

$$J_{00}c_0 + J_{01}c_1 = \beta . \qquad (3.12)$$

However, β is fixed by the requirement that $\tilde{C}(r) \rightarrow \cos(kr - \frac{1}{2}l\pi)$ (non-Coulomb case) as $r \rightarrow \infty$. This requirement yields[1,3]

$$\beta = -W/2s_0 , \qquad (3.13)$$

where again W is the r-space Wronskian of the regular and irregular solutions. Equation (3.13) fixes $\alpha(k)$, and we have finally

$$G_l^{0(+)}(n,n';k) = -(2/W) s_{n_<}(c_{n_>} + i s_{n_>}) . \qquad (3.14)$$

The correspondence with Eq. (3.2) could not be more complete. Simple substitution into Eq. (3.14) for any of the cases I–III listed in Sec. II provides the appropriate unperturbed J-matrix Green's function.

As further evidence that indeed

$$\langle \overline{\phi}_n | G_l^{0(+)} | \overline{\phi}_{n'} \rangle = -(2/W) s_{n_<}(c_{n_>} + i s_{n_>}) ,$$

we can work backwards from n space into r space, writing

$$G_l^{0(+)}(r,r';k) = -\frac{2}{W} \sum_{nn'} \phi_{n_<}(r) s_{n_<}(c_{n_>} + i s_{n_>}) \phi_{n_>}(r') .$$

Let us suppose that r' is large while r is small. Then the nature of the basis functions (i.e., their over-all coordinate space dependences as a function of n) dictates that only large n' contribute to $\phi_{n'}(r')$, while small n contribute to predominantly to $\phi_n(r)$. Thus, this heuristic argument allows us to write

$$\begin{aligned} G_l^{0(+)}(r,r';k) &\cong -\frac{2}{W}\left[\sum_n s_n \phi_n(r)\right] \times \left[\sum_{n'} (c_{n'} + i s_{n'}) \phi_{n'}(r')\right] \\ &= (-2/W) S(r)[C(r') + iS(r')] \end{aligned}$$

since contributions to the equation above for $n \geqslant n'$ are small.

Turning now to the full Green's functions, we want to find

$$G_l^{N(+)}(n,n';k) \equiv \langle \overline{\phi}_n | (J^{(+)} + V^N)^{-1} | \overline{\phi}_{n'} \rangle , \qquad (3.15)$$

or equivalently to solve

$$\sum_{n''} (J_{nn''} + V_{nn''}^N) G_l^{N(+)}(n'',n';k) = \delta_{nn'} . \qquad (3.16)$$

The J-matrix *wave function* which solves $(J + V^N)\psi = 0$ and which goes asymptotically as

$$\psi \rightarrow \cos\delta \sin(kr - \tfrac{1}{2}l\pi) + \sin\delta \cos(kr - \tfrac{1}{2}l\pi) \qquad (3.17)$$

(with a similar expression in the Coulomb case) we designate the *regular* full wave function ψ_{reg}. Similarly, we can imagine obtaining an irregular wave function ψ_{irreg} which goes asymptotically like

$$\psi_{\text{irreg}} \to \sin\delta \sin(kr - \tfrac{1}{2}l\pi) + \cos\delta \cos(kr - \tfrac{1}{2}l\pi)\,, \tag{3.18}$$

where δ is the same as in Eq. (3.17). The irregular J-matrix wave function can be obtained, in analogy with the problem of obtaining the cosine-like solution for the zero-order Hamiltonian H_l^0, by solving

$$(J + V^N)\psi_{\text{irreg}} = \gamma\bar{\phi}_0\,, \tag{3.19}$$

where the asymptotic form (3.18) is imposed with δ *fixed* from Eq. (3.17), and γ to be determined so that (3.19) and (3.18) are satisfied. The Eq. (3.19) leads to a J-matrix problem similar to the usual equations for the wave function ψ_{reg}, where now γ appears (instead of $t = \tan\delta$) as the $(N+1)$st unknown in the set $\{a_n, \gamma\}$; so that ψ_{irreg} has the expansion

$$\psi_{\text{irreg}} = \sum_{n=0}^{N-1} a_n\phi_n + \sin\delta S(r) + \cos\delta C(r)$$

$$\equiv \sum_{n=0}^{\infty} I_n\phi_n\,. \tag{3.20}$$

The reader may naturally suppose that armed with ψ_{irreg} and $\psi_{\text{reg}} \equiv \sum_{n=0}^{\infty} R_n\phi_n$ one can construct the full Green's function as

$$G_l^{N(+)}(n, n'; k) = -(2/W)R_{n_<}(I_{n_>} + iR_{n_>}) \tag{3.21}$$

in analogy with the coordinate space form, for a Hamiltonian $H_l^0(r) + V(r)$,

$$G_l^{(+)}(r, r'; k) = -(2/W)R(r_<)[I(r_>) + iR(r_>)]\,, \tag{3.22}$$

where W is the Wronskian of the regular and irregular solutions. Unfortunately, for n *and* $n' \le N-1$, this is not the case. The reason is that the potential $V_{nn'}^N$ is nonlocal (i.e., has off-diagonal elements) in the n indices. This spoils the "less-than, greater-than" prescription, as the reader may verify. The same is true in r space where a nonlocal potential $V(r, r')$ appears in the Hamiltonian: the form (3.22) no longer holds.

However, it is easily shown, along the lines of the arguments given for the unperturbed Green's functions, that Eq. (3.21) satisfies Eq. (3.16) if n *or* n' is greater than $N-1$. This is the region where the off diagonal potential V^N vanishes, allowing the simple result given in Eq. (3.21).

For n and $n' \le N-1$, we have to do a little more work to find $G_l^{N(+)}(n, n'; k)$. For fixed $n' \le N-1$, we write

$$G_l^{N(+)}(n, n'; k) = g_{nn'}\,, \quad n, n' \le N-1$$

$$= -(2/W)R_{n_<}(I_{n_>} + R_{n_>})\,, \quad n \text{ or } n' > N-1\,. \tag{3.23}$$

Equation (3.21) works for all but the N^2 elements $g_{nn'}$, which we find by solving the equations generated by inserting the form (3.23) into (3.16). These equations read

$$(J + V^N)g = 1 + b\,, \tag{3.24}$$

where

$$b_{nn'} = -(2/W)\delta_{N-1,\,n}J_{N-1,\,N}R_{n'}(I_N + iR_N)\,.$$

In Eq. (3.24), all quantities are $N\times N$ matrices (1 stands for the $N\times N$ unit matrix). Solving this matrix problem, we have the desired elements $g_{nn'} = G_l^{N(+)}(n, n'; k)$ for $n, n' \le N-1$. Remembering that J is a matrix composed of elements of $H_l^0 - E$ in the basis, we can avoid having to resolve Eq. (3.24) for each desired energy E by using the same prediagonalization technique used in Ref. 1 for the wave function.

This completes our analysis for the matrix elements of G_l^0 and G_l^N in the J-matrix L^2 basis, and we turn to applications in the following two sections.

IV. APPLICATION TO ATOMIC POLARIZABILITIES

The usual expressions for atomic polarizabilities (see below) can be written as L^2 matrix elements of Green's functions. Since we now have the necessary tools in hand to obtain such elements in analytic form, we can proceed to the J-matrix polarizability analysis. In keeping with the single-channel discussion of the previous sections, we speak here in terms of one-electron or one-electron-plus-core systems. An interesting and potentially very useful result of the analysis will be that a complete Rydberg series of poles in the frequency-dependent polarizability will appear in the J-matrix results independent of the number of basis functions used to describe the core potential. This is in contrast to the usual N-term variational results, which give N poles, whose positions, beyond the first few, have little to do with the physical resonant frequencies.

We first derive analytic results for the hydrogen atom, using the Coulomb J-matrix Green's functions derived in Sec. III. This is a "zero basis function" J-matrix calculation, since there is no potential in the problem other than those already accounted for analytically in the treatment of H_l^0. Following this, we indicate the modification needed to add a core pseudopotential.

The frequency-dependent polarizability $\alpha(\omega)$ of an atom can be written in terms of the quantities[16]

$$\alpha_\pm = \sum_{n=1}^{\infty} \frac{\langle 0|Z|n\rangle\langle n|Z|0\rangle}{E_n - E_0 \pm \omega}\,, \tag{4.1}$$

where $|0\rangle$ is the atomic state for which $\alpha(\omega) \equiv \alpha_+ + \alpha_-$ is the polarizability. The sum on n extends over all atomic states of the system, including the continuum, which connect with $Z|0\rangle$. For hydrogen, $Z = r\cos\theta$, and in the ground $1s$ state, only $l=1$ (p states) contribute, allowing us to write

$$\alpha_\pm = \langle \phi_{1s} | Z \tilde{G}_1^{0(+)}(r, r'; k_\pm) Z | \phi_{1s} \rangle \tag{4.2}$$

where $\tilde{G}_1^{0(+)}$ is the $l=1$ Coulomb Green's function. For frequencies of interest, below the ionization threshold, $k_\pm = [2(E_0 \mp \omega)]^{1/2}$ is purely imaginary, so we define $i\mu_\pm \equiv k_\pm$ for convenience. The outgoing scattering Green's function $\tilde{G}_1^{0(+)}(r, r'; k)$ for real positive k goes over to the correct exponentially damped Green's function $\tilde{G}_1^{0(+)}(r, r'; i\mu_\pm)$ for positive imaginary $k_\pm$. The Green's function appearing in Eq. (4.2) corresponds, of course, to the hydrogenic Hamiltonian

$$H_1^0 = -\frac{1}{2r^2}\frac{d}{dr} r^2 \frac{d}{dr} + \frac{1}{r^2} - \frac{1}{r}. \tag{4.3}$$

However, the J-matrix Green's function elements we have derived correspond to the Ricatti form of the kinetic energy, $-\frac{1}{2}d^2/dr^2$. Using the Ricatti Green's function $G_1^{0(+)}$, Eq. (4.2) becomes

$$\begin{aligned}\alpha_\pm &= \int\int\int d\Omega\, dr\, dr'\, \phi_{1s}(r) r^2 \cos\theta \\ &\quad \times G_1^{0(+)}(r, r'; i\mu_\pm) r'^2 \cos\theta\, \phi_{1s}(r') \\ &= \frac{4}{3}\int\int dr\, dr'\, r^2 e^{-r} G_1^{0(+)}(r, r'; i\mu_\pm) r'^2 e^{-r'} .\end{aligned} \tag{4.4}$$

Choosing a scaling parameter $\lambda = 2$ in the Laguerre basis set, Eqs. (3.5), we find that

$$r^2 e^{-r} = 3[\overline{\phi}_0(2r) - \overline{\phi}_1(2r)]. \tag{4.5}$$

From Eqs. (4.4) and (4.5), it is seen that $\alpha_\pm$ is expressed in terms of a few matrix elements,

$$\begin{aligned}\alpha_\pm = \tfrac{4}{3} \times 9 \times [&G_1^{0(+)}(0, 0; i\mu_\pm) \\ &- 2G_1^{0(+)}(0, 1; i\mu_\pm) + G_1^{0(+)}(1, 1; i\mu_\pm)].\end{aligned} \tag{4.6}$$

From Eqs. (2.11) and (3.14) with $i\mu_\pm = k_\pm$ we get

$$\begin{aligned}G_l^{0(+)}(n, n'; i\mu_\pm) = &-\frac{2n_< !\,|\Gamma(l+1+Z/\mu_\pm)|\sin\theta_\pm}{i\mu_\pm \Gamma(n_< + 2l + 2)} \\ &\times P_{n_<}^{l+1}(\cos\theta_\pm, 2Z/\lambda, -2Z/\lambda)\frac{n_> !\, e^{-i(n_>+1)\theta_\pm}}{\Gamma(n_> + l + 2 + Z/\mu_\pm)}\, {}_2F_1(-l + Z/\mu_\pm, n_> + 1; n_> + l + 2 + Z/\mu_\pm, e^{-2i\theta_\pm}),\end{aligned}$$

where

$$e^{i\theta_\pm} = -\left(\frac{\frac{1}{2} + \mu_\pm/\lambda}{\frac{1}{2} - \mu_\pm/\lambda}\right), \tag{4.7}$$

and $l=1, \lambda=2, Z=-1$ for the hydrogen ground-state polarizability. Equations (4.7) and (4.6) provide an analytic result for the frequency dependent polarizability of hydrogen. Similar solutions have been provided previously[17] by direct integration of the necessary matrix elements of the Coulomb Green's function.

As a check on our results, we take the $\omega \to 0$ limit and compare with the known value of $\alpha(\omega = 0) = \frac{9}{2}$. We find that $G_1^{0(+)}(0, 1, i) = 0$, $e^{i\theta} \to 0$, and we obtain further

$$G_1^{0(+)}(1, 1; i) = \tfrac{1}{48}, \quad G_1^{0(+)}(0, 0; i) = \tfrac{1}{6} .$$

Thus,

$$\begin{aligned}\alpha &= 2 \times \tfrac{4}{3} \times 9(\tfrac{1}{6} + \tfrac{1}{48}) \\ &= \frac{9}{2} .\end{aligned} \tag{4.8}$$

Note the poles in $G_1^{0(+)}(n, n'; i\mu)$ at the p-state hydrogenic energies, arising from the term in the numerator $|\Gamma(2 - 1/\mu)|$, $(l=1, Z=-1)$.

If we now add a pseudopotential to our one-electron problem (which would be one way of approximating alkali-metal atomic polarizabilities, for example), the Hamiltonian reads

$$H = -\frac{1}{2}\frac{d^2}{dr^2} + V_{p,l}(r) + \frac{l(l+1)}{2r^2} + \frac{Z}{r}. \tag{4.9}$$

We have allowed the pseudopotential $V_{p,l}(r)$ to depend on l; this would allow separate fits to the energy (and thus the asymptotic form) of the initial state and the pole positions (energies) of the states of differing symmetry which contribute to the polarizability. The importance of these parameters for static polarizabilities has been emphasized and demonstrated in the analytic theory and calculations of Adelman and Szabo.[18]

Several modifications of the theory given above are needed when an additional potential not present in H^0 is added. The pseudopotential must be truncated in the $N \times N$ matrix sense, leading of course to the appearance of J-matrix full of Green's functions $G_l^{N(+)}$ in the polarizability expressions, e.g.,

$$\alpha_\pm = \langle \phi_{\overline{1s}} | Z G_1^{N(+)} Z | \phi_{\overline{1s}} \rangle . \tag{4.10}$$

Further, in the example (4.10), for instance, the state $\phi_{\overline{1s}}$ is a ground s state in the presence of the $l=0$ pseudopotential $V_{p,0}$ and cannot be represented in general as the sum of just one or two J-matrix basis functions. In fact, to account properly for the important asymptotic behavior of $\phi_{\overline{1s}}$, it is necessary that a sufficient number of terms be included in the sum

$$\alpha_{\pm} \cong \sum_{nn'} \langle \phi_{\overline{1s}} | Z | \phi_n \rangle G_1^{N(+)}(n, n'; i\mu_{\pm}) \langle \phi_{n'} | Z | \phi_{\overline{1s}} \rangle . \tag{4.11}$$

Of course, it is also required that the approximation used to generate $\phi_{\overline{1s}}$ do justice to the correct asymptotic form of this function. If $\phi_{\overline{1s}}$ is a J-matrix *bound state*, then it is of the form[19]

$$\begin{aligned} \phi_{\overline{1s}} &= \sum_{n=0}^{\infty} a_n \phi_n \\ &\equiv \sum_{n=0}^{N-1} a_n \phi_n + b e(r) , \end{aligned} \tag{4.12}$$

where asymptotically $e(r)$ satisfies H_l^0, thus assuring the correct long-range behavior of $\phi_{\overline{1s}}$. The coefficients a_n appearing in

$$b e(r) \equiv \sum_{n=N}^{\infty} a_n \phi_n \tag{4.13}$$

decrease exponentially with n for bound states,[19] and this implies that the sums over n and n' in Eq. (4.11) will converge rapidly after a certain number of terms. Note that each term in Eq. (4.11) carries with it the full Rydberg singularity structure present in $G_1^{N(+)}(n, n'; i\mu_{\pm})$ (for H_l^0 which are asymptotically Coulomb). The lowest-energy poles in $G_1^{N(+)}$ will be perturbed from a perfect Coulomb Rydberg series as a result of the presence of V_P^N; for large quantum numbers this will settle into a simple quantum-defect behavior.

To find $G^N(n, n'; i\mu_{\pm})$ requires an $N \times N$ matrix diagonalization. This is the same effort as in the N-term variational treatment of polarizabilities,[16] but in the J-matrix approach we get not N "pseudopoles" but a complete Rydberg series. The Rydberg series of poles is accounted for in the J-matrix approach because the Coulomb-H^0 Hamiltonian is treated exactly. Since this Hamiltonian dominates asymptotically, the Rydberg series is present. It should be noted, however, that this has little effect on atomic properties dependent on $\alpha(\omega)$ for ω lying far from the "inaccurate" variational poles, since the variational pseudopole sums perform well under such circumstances.

It is interesting to compare the J-matrix approach to polarizabilities treated above to the numerical method of Alexander and Gordon.[20] These authors directly solve the Schrödinger equation for the first-order wave function $\tilde{\phi}^{\pm}$ in the presence of an harmonic time-dependent perturbation, $\exp(i\omega t)\tilde{W}(r) + \exp(-i\omega t)\tilde{W}(r)$, i.e.,

$$(H^0 + \tilde{V} + E_0 \pm \omega)\tilde{\phi}^{\pm} = -\tilde{W}\psi_0 , \tag{4.14}$$

where $H^0\psi_0 = E_0\psi_0$. In Eq. (4.14), $\tilde{V}$ and $\tilde{W}$ are piecewise linear fits to the exact potential $V(r)$ and perturbation $W(r)$. Then quantities such as $\alpha_{\pm}$, are computed as usual from

$$L^{\pm}(\omega) = \langle \tilde{\phi}^{\pm} | \tilde{W} | \psi_0 \rangle , \tag{4.15}$$

where $\alpha_{\pm} = L^{\pm}$ for $W = r\cos\theta$. This approach also enjoys the advantage that the anomalous dispersion region is correctly treated. In fact, our results could also have been cast in the form (4.14), (4.15) where now $\tilde{V}$ and $\tilde{W}$ become V^T and W^T, the truncated $N \times N$ matrix approximations in the J-matrix basis set. It is felt that the J-matrix approach has some advantages over coordinate-space techniques, however, since nonlocal potentials (such as those which occur in the coupled Hartree-Fock equations) are more easily treated by basis set methods and since the result is given in analytic form for all ω in terms of the parameters of a single matrix diagonalization. The J-matrix approach thus combines some of the best qualities of the variational and "numerical" methods.

V. APPLICATION TO ERROR BOUNDS FOR J-MATRIX PHASE SHIFTS

The Kato identity[4]

$$\begin{aligned} \tan\delta = \tan\delta_t &- (2/k)\langle \psi_t | H - E | \psi_t \rangle \\ &+ (2/k)\langle \Delta\psi | H - E | \Delta\psi \rangle \end{aligned} \tag{5.1}$$

serves as a basis for many theoretical treatments of phase-shift error bounds. In Eq. (5.1), δ is the exact phase shift and ψ is the exact wave function at energy E for the Hamiltonian H, ψ_t is a "trial" wave function behaving as $\psi_t \rightarrow \sin kr + \tan\delta_t \cos kr$ $(r \rightarrow \infty)$, and $\Delta\psi \equiv \psi_t - \psi$. The term $(2/k)\langle \psi_t | H - E | \psi_t \rangle$ serves as a useful "Kato correction" to the initial value for the tangent of the phase shift, $\tan\delta_t$. An appropriate bound for the term $(2/k)\langle \Delta\psi | H - E | \Delta\psi \rangle$ must be found in order to bound the difference between $\tan\delta$ and $\tan\delta_t$, and discussions about error bounds naturally center around this term. Our treatment will deviate slightly from this in that, because of the nature of the J-matrix "trial" function, we can use a simplified form for Eq. (5.1), namely

$$\begin{aligned} \tan\delta &= \tan\delta_N - (2/k)\langle \psi^N | V^R | \psi^N \rangle + (2/k)\langle \Delta\psi | H - E | \Delta\psi \rangle \\ &= \tan\delta_N - (2/k)\langle \psi^N | V^R | \psi \rangle , \end{aligned} \tag{5.2}$$

where

$$(H_l^0 + V^N)\psi^N = 0 \tag{5.3}$$

and

$$H_l = H_l^0 + V^N + V^R$$

Our problem of bounding the difference $|\tan\delta - \tan\delta_N|$ reduces to that of bounding the last term in Eq. (5.2). The last line of Eq. (5.2) is simply a version of the two-potential formula, where $V^N + V^R = V$. We are taking advantage in Eq. (5.2) of the fact that the J-matrix wave functions are exact solutions of well-defined scattering problems [Eq. (5.3)].

The task of bounding the term $(2/k)\langle\psi^N | V^R | \psi\rangle$ involves techniques introduced into scattering theory by Scadron and Weinberg[21] in the course of the development of the quasiparticle method. The approach is quite simple to outline for the J-matrix case which we do in the steps below.

The discussion is facilitated if we work with wave functions of somewhat different normalization than those of Eqs. (5.1) and (5.2). We define

$$\begin{aligned}\tilde\psi^N &\to \sin(kr + \delta_N)\\ \tilde\psi &\to \sin(kr + \delta_N) + \tan(\delta - \delta_N)\cos(kr + \delta_N)\,,\end{aligned}\qquad (5.5)$$

which differ from ψ^N and ψ by over-all factors. With these definitions we have

$$\begin{aligned}\tilde\psi &= \tilde\psi^N + G^N V^R \tilde\psi\\ &\to \sin(kr + \delta_N) - (2/k)\langle\tilde\psi^N | V^R | \tilde\psi\rangle\cos(kr + \delta_N)\end{aligned}\qquad (5.6)$$

where G^N is the full principal-value J-matrix Green's function. Thus, from Eqs. (5.5) and (5.6),

$$\tan(\delta - \delta_N) = -(2/k)\langle\tilde\psi^N | V^R | \tilde\psi\rangle \qquad (5.7)$$

and

$$\begin{aligned}|\tan(\delta - \delta_N)| &= (2/k)\,|\langle\tilde\psi^N | V^R | \tilde\psi\rangle|\\ &\leqslant (2/k)\,|\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle + \langle\tilde\psi^N | V^R G^N V^R | \tilde\psi^N\rangle + \langle\tilde\psi^N | V^R G^N V^R G^N V^R | \tilde\psi^N\rangle + \cdots|\\ &\leqslant (2/k)\{|\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle| + |\langle\tilde\psi^N | V^R G^N V^R | \tilde\psi^N\rangle| + \cdots\}\\ &\leqslant (2/k)\{|\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle| + \|\langle\tilde\psi^N | (V^R)^{1/2}\|^2\, \|(V^R)^{1/2} G^N (V^R)^{1/2}\|\\ &\qquad + \|\langle\tilde\psi^N | (V^R)^{1/2}\|^2\, \|(V^R)^{1/2} G^N (V^R)^{1/2}\|^2 + \cdots\}\\ &= (2/k)\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle\{1/(1 - \|K\|)\}\end{aligned}\qquad (5.8)$$

where $K = (V^R)^{1/2} G^N (V^R)^{1/2}$.
The symbol $\|\cdots\|$ stands for a vector or operator norm,[22] as the case may be. Similarly, it may be shown that

$$|\tan(\delta - \delta_N) + (2/k)\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle| \leqslant (2/k)\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle\{\|K\|/(1 - \|K\|)\}. \qquad (5.9)$$

The advantage of the symmetric form for K is that it is an L^2 operator, i.e.,

$$\begin{aligned}\|K\|^2 &= \mathrm{Tr}K^\dagger K = \mathrm{Tr}(V^R)^{1/2} G^N V^R G^N (V^R)^{1/2}\\ &= \mathrm{Tr}(G^N V^R G^N V^R) < \infty\,,\end{aligned}\qquad (5.10)$$

where Tr is the quantum trace operation. Provided we can calculate $\|K\|$ and $\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle$, and that $\|K\| < 1$, Eqs. (5.8) and (5.9) provide the desired bounds. The term $\langle\tilde\psi^N | V^R | \tilde\psi^N\rangle$ is just the Kato correction term and can be computed by writing

$$\tilde\psi^N = \left(\sum_{n=0}^{N-1} a_n \phi_n\right)\cos\delta_N + \cos\delta_N S(r) + \sin\delta_N C(r)$$

and $V^R = V - V^N$. By using the explicit r-dependent forms for $S(r)$ and $C(r)$,[1-3] $\langle\tilde\psi_N | V^R | \tilde\psi_N\rangle$ is obtainable in terms of certain bound-bound, bound-free, and free-free integrals. Computation of

$$\|K\|^2 = \mathrm{Tr}(G^N V^R)^2 = \sum_{n,n'} (G^N V^R)^2_{nn'}\,, \qquad (5.11)$$

requires knowledge of the J-matrix Green's function (Sec. III). We note the following facts about $\|K\|$: (i) As the number of basis functions used for V^N gets larger, $V^R \equiv V - V^N$ gets "smaller," and $\|K\|$ is expected to follow suit. (ii) Near resonances for the Hamiltonian $H^0 + V^N$, G^N will get "larger" due to a nearby second-sheet pole in the complex energy plane,[23] and $\|K\|$ is expected to follow suit. (iii) In going from $E = \infty$ toward $E = 0$, if $H^0 + V$ possesses a resonance not present in $H^0 + V^N$, then $\|K\|$ will become greater than unity, and there will be no bound on $\tan(\delta - \delta_N)$, in accord with a phase-shift error of π due to the missing resonance. This phenomenon is, of course, related to the failure of the distorted-wave Born series, Eq. (5.8), to converge in this case.

In practice, it may be difficult to obtain an exact result for $\|K\|^2$. However, for some potentials V^R it may be possible to find M such that

$$\|K\|^2 \leqslant \sum_{n,n'} \left(\sum_m |G^N_{nm} V^R_{mn'}|\right)^2 \leqslant M < 1\,, \qquad (5.12)$$

but others may depend too sensitively on sign cancellation in the sum

$$\sum_{m} G^{N}_{nm} V^{R}_{mn'} .$$

In this case a useful estimate of $\|K\|$ may be obtained by summing Eq. (5.11) numerically (until a reasonably well-converged result is obtained) or by other means.

The clear implication of the analysis is that provided $\|K\| < 1$, no false pseudoresonances can appear in the J-matrix method. For a large enough $N \times N$ matrix V^N, $\|K\|$ will always be less than unity. For electron-atom collisions at least, it appears that the size of N needed to assure a lack of pseudoresonances is small indeed. Using very small basis sets and fine energy searches such a false resonance has not occurred in J-matrix work. Of course, even if $\|K\| > 1$ there is no *requirement* that pseudoresonances should occur.

VI. SUMMARY

We have extended the J-matrix scattering theory to include construction of appropriate L^2 matrix elements of unperturbed and full J-matrix Green's functions. These Green's functions were in turn used in applications to the J-matrix approach to atomic-frequency dependent polarizabilities and to establishment of error bounds and a discussion on the lack of pseudoresonances in J-matrix phase shifts.

The fully analytic nature of the J-matrix approach to scattering, and the fact that this approach does no violence to the operator H^0 responsible for continuous spectra, Rydberg series, etc. has made the analysis possible.

It is worth reemphasizing here that the J-matrix methods, together with the R-matrix approach,[24] are the only easily *calculable* specific realizations of the general Feshbach formalism for scattering.[25] In both R- and J-matrix theories, the operator $H_{PQ} = H^0_{PQ}$ (in Feshbach's language) has simple structure (albeit in quite different Hilbert spaces), permitting analytic results. In the R-matrix approach H^0_{PQ} is manifested in the Bloch $\mathcal{L}$ operator, whereas in J-matrix theory H^0_{PQ} has but one nonzero element. This simple structure of the unperturbed Hamiltonian, together with the solubility of the H_{QQ} and H^0_{PP} problems, makes both R- and J-matrix work analytically tractable.

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[15] In our applications, either $\phi_n = \overline{\phi}_n$ (oscillator basis) or $\phi_n(r) = \mu r \overline{\phi}_n(r)$, where μ is a constant (Laguerre basis). Since the difference between ϕ_n and $\overline{\phi}_n$ is n independent, we may still write

$$1 = \sum_{n} |\overline{\phi}_n\rangle\langle\phi_n| = \sum_{n} |\phi_n\rangle\langle\overline{\phi}_n|$$

for J-matrix purposes. This construct is just a shorthand way of the usual procedure of expanding ψ^N in the complete set $\{\phi_n\}$, inserting into Eq. (2.14), for example, and multiplying from the left by all $\langle\phi_n|$. The resulting equations are identical to those generated with our unorthodox unit operator.

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