Extension of time-independent wave-operator methods to the calculation of the two-body Coulomb photoionization amplitude

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A finite-basis method [B. R. Johnson and W. P. Reinhardt, Phys. Rev. A **28**, 1930 (1983)] recently introduced for calculating bound-free transition amplitudes is extended here to apply to the Coulomb potential. This method is based upon the use of complex-coordinate techniques to calculate matrix elements of the time-independent wave operators of formal scattering theory, and avoids explicit enforcement of coordinate-space boundary conditions. Numerical experiments aiming at the calculation of the known hydrogenic ground-state photoionization amplitude have been made with use of different known forms of the two-body Coulomb wave operator. We have successfully reproduced the hydrogenic photoionization amplitude, but only within an accuracy and precision of about 1%. The most plausible explanation for these numerical difficulties is associated with the singular behavior of the "$i\varepsilon$" limit in Coulomb scattering theory. In shorter-range problems, this limit is conveniently implemented by complex-coordinate techniques or complex-coordinate techniques in conjunction with Padé extrapolation. However, neither of these methods effectively implements the $\varepsilon \rightarrow 0$ limit in the Coulomb case.

I. INTRODUCTION

A new method has recently been introduced[1] for the construction of bound-free transition amplitudes in a broad range of systems. This requires the calculation of matrix elements of Møller wave operators,[2–4] and has the promising features of using only finite-basis techniques while automatically satisfying the asymptotic boundary conditions on the scattering wave function. The first calculations demonstrated the feasibility of the method for both short-range (exponentially decaying) and long-range ($-1/r^4$) single-channel problems. This provides real encouragement for the extension to multichannel and Coulomb scattering problems. This paper describes attempts to numerically calculate bound-free amplitudes for the Kepler problem. This differs from the previous single-channel examples in that the wave operators for interactions of charged particles are well-known to be of a qualitatively different form.[5–12]

The incentive for the pursuit of the present wave-operator methods is the hope that partial scattering amplitudes can be obtained even when a large, potentially infinite, number of open channels are present. One specific application we have in mind is the double-electron photoionization amplitude for H^- above the three-body breakup threshold,[13] a region for which there do not as yet exist systematic computational methods since the detailed specification of the three-body Coulomb asymptotic form has not been given. In this case the fact that explicit coordinate-space boundary conditions need not be enforced in the finite L^2 basis calculation would be used advantageously. Another planned application is in the calculation of electronic amplitudes for molecular photoionization in the adiabatic nuclei approximation.[14] This would allow calculation of electron angular distributions, in addition to the total cross sections, which are currently calculable via moment imaging techniques.[15]

The use of wave operators is very straightforward in principle. We take $|1s\rangle$ to be the ground-state hydrogenic wave function and $|\mathbf{k}\pm\rangle$ to be the three-dimensional Coulomb continuum wave function for an ionized electron of momentum $\mathbf{k}$. The superscript $+$ $(-)$ denotes a state asymptotically prepared in the past (future). The transition matrix element describing ionization by a photon of frequency ω (fixed by energy conservation) is then given by[16]

$$A(\mathbf{k}) = -i\frac{\omega^{1/2}}{2\pi}\langle \mathbf{k}- | \boldsymbol{\varepsilon}\cdot\mathbf{D} | 1s\rangle \ . \tag{1.1}$$

Here $\mathbf{D}$ is the dipole moment operator and $\boldsymbol{\varepsilon}$ the polarization vector. The continuum wave function can be expressed formally as

$$|\mathbf{k}\pm\rangle = \Omega^{(\pm)}|\mathbf{k}\rangle \ , \tag{1.2}$$

where $\Omega^{(\pm)}$ is a Coulomb wave operator and $|\mathbf{k}\rangle$ is a free-particle state. When operating upon $|\mathbf{k}\rangle$, $\Omega^{(\pm)}$ can be expressed in different forms involving the resolvent

$$G(E\pm i\varepsilon)=(E\pm i\varepsilon-H)^{-1}\,, \tag{1.3}$$

of the internal two-body Coulomb Hamiltonian H. Complex-coordinate techniques for calculating matrix elements of resolvents[1,17–19] can then be exploited, facilitating the necessary implementation of the limit $\varepsilon\to 0$. The key to the success of this approach is the fact that the matrix element A is damped exponentially by the presence of the bound-state wave function. Thus good approximations to the resolvent are required only over localized regions of coordinate space.

We show that use of one of the standard forms of the wave operator from the scattering theory of shorter-range potentials leads to very stable *partial* results in the computation of the ground-state hydrogenic photoionization amplitude. This provides encouragement that the finite-basis methods can indeed be adapted to transition amplitudes for Coulomb problems. It is *not* possible to recover the complete amplitude in this manner, however, because the shorter-range wave operator is simply inappropriate to Coulomb potentials. This is manifested by the appearance in the resulting amplitude of the phase factor $\varepsilon^{\mp iZ/k}$, where Z is the nuclear charge. This factor is ill-behaved in the limit $\varepsilon\to 0$. The same difficulty is well-known in the context of the scattering amplitude for the two-body problem, and also appears when more charged fragments are present. For N-particle Coulomb systems, Zorbas[9] has given a generalization of the wave operator which explicitly contains the inverse of the corresponding ill-behaved phase factor. Computations based on this operator do not suit our purpose, however, in that we are seeking a stable numerical method for determining matrix elements of the continuum wave functions (with the correct normalization and phase) without singularities as the real energy axis is approached.

Within time-dependent scattering theory, it was shown by Dollard[5] that wave operators for Coulomb scattering could be obtained which contain extra terms over those in the shorter-range case. It has been shown subsequently by Gibson and Chandler[8] that Dollard's results, when transformed into the time-independent framework, lead naturally to an operator involving a complex power of the resolvent. (See also Refs. 7, 9, 11, and 12 for related work.) This complex power is no real complication for our numerical methods, and so attempts were made to obtain the photoionization amplitude using the wave operator corresponding to the work of Gibson and Chandler. While these efforts were successful, there is unfortunately a substantial sensitivity to the parameters used in the finite-basis calculations, and nonsystematic convergence or even divergence seems to be the general rule. The best relative accuracy is approximately on the order of 1%. Should this prove to be an absolute limit on the accuracy available for a one-channel problem, it is unlikely that the Gibson-Chandler method would yield a practical tool for the much more difficult double photoionization problem.

There is a third wave operator, due to Mulherin and Zinnes,[6] which is more naturally suited to parabolic rather than spherical coordinates. This operator has the advantage of incorporating explicitly the leading asymptotic distortion of the plane wave by the Coulomb potential. (See also Refs. 20 and 21). This is in the spirit of distorted wave calculations, but with no approximations made. The problem thereby reduces to one involving operators which take into account the ultra-long-range Coulomb forces. Unlike the Gibson-Chandler and Zorbas operators, the Mulherin-Zinnes wave operator does not adapt readily to a partial-wave expansion, but this slight technical disadvantage can be overcome in the current application by projecting out the relevant partial wave.[22] The numerical results do indeed represent a small improvement over those from the Gibson-Chandler operator, but not a dramatic improvement.

Several other numerical experiments were made in attempts to obtain higher accuracy. One finding was that taking the wave operators off the energy shell (i.e., using a finite value of ε) causes the resulting amplitudes to converge very rapidly. The finite-basis methodology is therefore capable of calculating the necessary matrix elements extremely well, but only at unphysical complex values of the energy. Furthermore, attempts to extrapolate well-converged off-shell amplitudes back to the real energy axis also failed to lead to greater accuracy than the primitive real-axis calculations. We now consider these difficulties to be related to those discussed by McCartor and Nuttall[23] in extrapolating T-matrix amplitudes for Coulomb scattering from the complex energy plane on to the real axis. The problem for any of the wave operators used is apparently due to a pathological behavior of the function calculated in the $i\varepsilon$ limit. It is important to remark that this is transparently so for the Zorbas operator, but not for the others. In fact, our previous work for non-Coulombic interactions had led us to hope that the other operators would readily lend themselves to simple, stable computational procedures.

Another point arising from the experiments with finite ε is that the use of complex scaling actually *destabilizes* the convergence of the off-shell amplitudes. The usual experience[1,18,19] in bound-bound and shorter-range bound-free amplitudes is that the scaling allows one to effectively avoid the poles occurring on the real axis in the finite-basis approximation to the resolvent, thereby stabilizing the results. On the other hand, in the off-shell amplitudes, where the poles are avoided automatically, the optimal value of the rotation angle is found to be zero or very close to zero, with larger values resulting in amplitudes which diverge as the basis size increases. Not only is the use of complex coordinates unnecessary in this context, but it actually appears to be deleterious. This will be discussed in more detail below.

The quality of the results obtained by the above methods must be judged in terms of intended use. For the problem of single-channel atomic or molecular photoionization a promising new method for calculation of amplitudes may be at hand. Some numerical study will be necessary to verify that in this case the combination of short-range correlation and long-range Coulomb effects are correctly described in this method. If the numerical inaccuracies should prove to be comparable in one-channel and multichannel photoionization, then the procedures outlined here would warrant further investigation. However, viewed as a step towards calculating double

photoionization amplitudes, it is likely to be a far more difficult numerical procedure. The methods developed in these initial efforts would not warrant a full-scale computational attack on the two-electron continuum.

The organization is the following. In Sec. II the methods used in Ref. 1 for standard scattering problems is reviewed. In Sec. III, the necessary operators and wave functions for the two-body Coulomb problem are summarized. The Zorbas operator is treated in Sec. IV, the Gibson-Chandler operator in Sec. V, and the Mulherin-Zinnes operator in Sec. VI. Section VII contains a discussion. Analytic results connecting the Zorbas and Gibson-Chandler operators are sketched in an Appendix.

II. NON-COULOMB WAVE-OPERATOR METHODS

In our previous paper,[1] we showed that it is possible to use complex-coordinate techniques[14–16] to calculate bound-free matrix elements of the form $\langle \Phi_{\text{bound}} | \mathbf{k}\pm \rangle$, where Φ_{bound} is a function which decays exponentially with r and $|\mathbf{k}\pm\rangle$ is the continuum state appropriate to a Hamiltonian

$$H=H_0+V \ . \tag{2.1}$$

Here H_0 is a free-particle Hamiltonian and V is a potential decaying faster at infinity than $1/r$. The scattering function can be obtained by application of the Møller wave operator[2–4] to a plane wave, as indicated in Eq. (1.2). Within time-dependent scattering theory, these operators are expressed (with $\hbar=1$) as

$$\Omega^{(\pm)}=s-\lim_{t\to\mp\infty}\exp(iHt)\exp(-iH_0t) \ . \tag{2.2}$$

Equations (1.2) and (2.2) correspond to propagating the free-particle wave function backward (forward) in time until the scattering potential is completely turned off, and then propagating it back to the present with the full Hamiltonian H.

In the time-independent picture with which we shall be working, the Møller operator may be recast in integral terms with a suitable convergence factor,[3,4,24]

$$\Omega^{(\pm)}=\varepsilon\int_0^\infty dt\, e^{-\varepsilon t}e^{\mp iHt}e^{\pm iH_0t} \ . \tag{2.3}$$

The strong limit $\varepsilon\to 0$ is implied in Eq. (2.3). Application to a plane-wave state then yields

$$\begin{aligned}\Omega^{(\pm)}|\mathbf{k}\rangle&=\varepsilon\int_0^\infty dt\, e^{-\varepsilon t}e^{\mp iHt}e^{\pm iH_0t}e^{\pm ik^2t/2}|\mathbf{k}\rangle\\&=\pm i\varepsilon(\tfrac{1}{2}k^2\pm i\varepsilon-H)^{-1}|\mathbf{k}\rangle\\&=[1+(\tfrac{1}{2}k^2\pm i\varepsilon-H)^{-1}V]|\mathbf{k}\rangle \ .\end{aligned} \tag{2.4}$$

The fact that $|\mathbf{k}\rangle$ is a solution of the free-particle wave equation with energy $E=k^2/2$ has been used in obtaining these identities. In terms of the resolvent of H, we shall frequently refer in the following to

$$\begin{aligned}\Omega^{(\pm)}&=\pm i\varepsilon G(E\pm i\varepsilon)\\&=1+G(E\pm i\varepsilon)V\end{aligned} \tag{2.5}$$

as standard forms of the Møller operators, with the understanding that they are operating upon the free-particle wave function.

If the potential V is spherically symmetric, one can make a partial-wave expansion of the plane wave $\Psi_0(\mathbf{k},\mathbf{r})$,

$$\begin{aligned}\Psi_0(\mathbf{k},\mathbf{r})&=(2\pi)^{-3/2}e^{i\mathbf{k}\cdot\mathbf{r}}\\&=\left[\frac{2}{\pi}\right]^{1/2}\frac{1}{kr}\sum_{l,m}i^l\psi_{l0}(kr)Y_{lm}(\hat{r})Y^*_{lm}(\hat{k}) \ ,\end{aligned} \tag{2.6}$$

where the radial function $\psi_{l0}(kr)$ is simply the regular function corresponding to energy E and radial Hamiltonian

$$h_{l0}=-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2} \ . \tag{2.7}$$

Similarly, the full three-dimensional wave function can be expanded as

$$\Psi^{(\pm)}(\mathbf{k},\mathbf{r})=\frac{1}{kr}\left[\frac{2}{\pi}\right]^{1/2}\sum_{l,m}i^l\psi_l^{(\pm)}(k,r)Y_{lm}(\hat{\mathbf{r}})Y^*_{lm}(\hat{\mathbf{k}}) \ , \tag{2.8}$$

with $\psi_l^{(\pm)}(k,r)$ corresponding to the radial operator

$$h_l=h_{l0}+V(r) \ . \tag{2.9}$$

The radial wave operator is then as in Eqs. (2.5), except that H is replaced by h_l. The last form is convenient for utilizing the coordinate-rotation method because ε only occurs in the combination $E\pm i\varepsilon$. Letting ϕ be a purely radial function, the matrix element $\langle\phi|\psi_l^{(\pm)}\rangle$ becomes

$$\langle\phi|\psi_l^{(\pm)}\rangle=\langle\phi|\psi_{l0}\rangle+\left\langle\phi\left|\frac{1}{E\pm i\varepsilon-h_l}V\right|\psi_{l0}\right\rangle \ . \tag{2.10}$$

The second integral can be subjected to the dilatation transformation $r\to re^{i\theta}$ with the result

$$\left\langle\phi\left|\frac{1}{E\pm i\varepsilon-h_l}V\right|\psi_{l0}\right\rangle=\left\langle\phi_\theta\left|\frac{1}{E\pm i\varepsilon-h_{l\theta}}V_\theta\right|\psi_{l0\theta}\right\rangle \ , \tag{2.11}$$

in terms of the rotated quantities

$$\phi_\theta(r)=e^{i\theta/2}\phi(re^{i\theta}) \ , \tag{2.12}$$

$$h_{l\theta}=e^{-2i\theta}h_{l0}+V_\theta(r) \ , \tag{2.13}$$

$$V_\theta(r)=V(re^{i\theta}) \ , \tag{2.14}$$

and

$$\psi_{l0\theta}(k,r)=e^{i\theta/2}\psi_{l0}(k,re^{i\theta}) \ . \tag{2.15}$$

The radial Hamiltonian $h_{l\theta}$ is next diagonalized in a convenient basis, in our applications the Laguerre basis

$$\Phi_{nl}(r)=\left[\frac{n!\lambda}{(n+2l+2)!}\right]^{1/2}(\lambda r)^{l+1}e^{-\lambda r/2}L_n^{2l+2}(\lambda r) \ . \tag{2.16}$$

For a given basis size N, this results in N complex eigenvalues $E_{i\theta}$ and eigenvectors $\chi_{i\theta}(r)$. The matrix element in Eq. (2.11) can then be approximated by

$$\left\langle \phi_\theta \left| \frac{1}{E\pm i\varepsilon - h_{l\theta}} V_\theta \right| \psi_{l0\theta} \right\rangle \cong \sum_{i=1}^{N} \frac{(\phi_\theta | \chi_{i\theta})(\chi_{i\theta} | V_\theta | \psi_{l0\theta})}{E\pm i\varepsilon - E_{i\theta}} , \tag{2.17}$$

where the parentheses indicate that there is to be no complex conjugation. This approximation of the resolvent Green's function by square-integrable functions is only expected to be valid over a localized region of configuration space, but this is the only region sampled in any case due to the presence of the bound-state function ϕ in the original matrix element. The importance of the coordinate rotation lies in the fact that the branch cut of the resolvent is swept down into the complex energy plane at an angle 2θ with respect to the positive real axis.[17] This allows one to take the $\varepsilon \to 0$ limit smoothly in each term of the sum in Eq. (2.17) with no danger of a vanishing denominator. The practical utility of this method has been demonstrated in our earlier examples.[1]

III. COULOMB WAVE FUNCTIONS AND PARTIAL WAVES

The properties of the hydrogenic functions needed below can be succinctly described. The discussion closely follows that of Newton[2] and the parallel description for shorter-range potentials in Ref. 1.

The attractive Coulomb Hamiltonian is given by

$$H = -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} , \tag{3.1}$$

where Z is the nuclear charge. The ground-state wave function for this Hamiltonian is

$$\chi_{1s}(\mathbf{r}) = \frac{1}{r} R_{1s}(r) Y_{00}(\hat{r}) , \tag{3.2}$$

where Y_{00} is a spherical harmonic and R_{1s} is the radial wave function

$$R_{1s}(r) = 2Z^{3/2} r e^{-Zr} . \tag{3.3}$$

The three-dimensional scattering function has the explicit form

$$\Psi^{(\pm)}(\mathbf{k},\mathbf{r}) = \frac{e^{\eta\pi/2}}{(2\pi)^{3/2}} \Gamma(1\mp i\eta) \times e^{i\mathbf{k}\cdot\mathbf{r}} {}_1F_1(\pm i\eta; 1; \pm i(kr \mp \mathbf{k}\cdot\mathbf{r})) , \tag{3.4}$$

where the ${}_1F_1$ is a confluent hypergeometric function and

$$\eta = Z/k . \tag{3.5}$$

The wave function $\Psi^{(\pm)}(\mathbf{k},\mathbf{r})$ has a partial wave expansion as in Eq. (2.8) with the radial function $\psi_l^{(\pm)}(k,r)$ given by

$$\psi_l^{(\pm)}(k,r) = \frac{(2kr)^{l+1}}{2} e^{\eta\pi/2} \frac{\Gamma(l+1\mp i\eta)}{\Gamma(2l+2)} e^{\pm ikr} \times {}_1F_1(l+1\mp i\eta; 2l+2; \mp 2ikr) , \tag{3.6}$$

Hereafter, we shall restrict discussion to $l=1$ and drop this index except when necessary for clarity.

In the examination of the Zorbas wave operator for the two-body problem, we shall also consider the individual spherical waves

$$f_\pm(k,r) = e^{-\eta\pi/2} W_{\pm i\eta,3/2}(\mp 2ikr) , \tag{3.7}$$

where the W's are Whittaker functions. These are the solutions of the radial equation which are irregular at the origin, and which have the following asymptotic behaviors:

$$f_\pm(k,r) \to (2kr)^{\pm i\eta} e^{\pm ikr} \text{ as } r \to \infty . \tag{3.8}$$

In terms of these functions, the physical wave function $\psi^{(+)}(k,r)$ is

$$\psi^{(+)}(k,r) = -\frac{1}{2}\left[f_-(k,r) + \frac{J_-(k)}{J_+(k)} f_+(k,r) \right] , \tag{3.9}$$

where the Jost functions $J_\pm(k)$ are given by

$$J_\pm(k) = e^{-\eta\pi/2}/\Gamma(2\mp i\eta) . \tag{3.10}$$

In the limit that the nuclear charge Z vanishes, the above radial functions reduce to the appropriate free-particle analogs:

$$f_\pm(k,r) \to f_{0\pm}(k,r) = -\hat{h}_1^{(1,2)}(kr) , \tag{3.11}$$

$$\psi^{(+)}(k,r) \to \psi_0^{(+)}(k,r) = \hat{j}_1(kr) . \tag{3.12}$$

Here $\hat{h}_1^{(1,2)}(kr)$ are spherical Riccati-Hankel functions, and $\hat{j}_1(kr)$ is the regular spherical Riccati-Bessel function mentioned in Eq. (2.6).

By use of Eq. (2.8) in (1.1), the Coulomb photoionization amplitude can be reduced to

$$A(\mathbf{k}) = -(2\pi)^{-2}(1+\eta^2)^{1/2} \boldsymbol{\varepsilon}\cdot\hat{\mathbf{k}} I(k) , \tag{3.13}$$

where the radial integral $I(k)$ is

$$I(k) = \int_0^\infty dr\, \psi^{(-)*} r R_{1s} . \tag{3.14}$$

Since $\psi^{(-)*}(k,r) = \psi^{(+)}(k,r)$ for real k, and $R_{1s}(r)$ is real, $I(k)$ can also be written in the convenient form

$$I(k) = \int_0^\infty dr\, R_{1s} r \psi^{(+)} , \tag{3.15}$$

adopted in the remainder of the paper. The integral I is straightforwardly evaluated in closed form:

$$I(k) = 8Z^{-3/2}\eta^4 e^{-\eta\pi/2} \frac{\Gamma(2-i\eta)}{(1+\eta^2)^3} \left[\frac{1-i\eta}{1+i\eta} \right]^{i\eta} . \tag{3.16}$$

This will provide us with an absolute standard for judging the numerical results of later sections. The helicity-averaged cross section is then given by[16]

$$\sigma = \frac{4\pi k}{3c}(1+\eta^2) |I(k)|^2 . \tag{3.17}$$

We will also have occasion to examine the individual contributions of $f_\pm(k,r)$ to $I(k)$. Thus we define

$$I_+(k)=\int_0^\infty dr\, R_{1s}(r) r f_+(k,r)/J_+(k)$$
$$=-\frac{192 i\eta^3\Gamma(2-i\eta)}{Z^{3/2}\Gamma(4-i\eta)(1+i\eta)^5}$$
$$\times {}_2F_1(5,2-i\eta;4-i\eta;(1-i\eta)/(1+i\eta)) . \quad (3.18)$$

We have taken the simple expedient in computing this amplitude of summing the Gauss hypergeometric series via Padé approximants.[25] Inspection of Eq. (3.9) gives the explicit connection between $I_+(k)$ and $I(k)$,

$$I(k)=-J_-(k)\mathrm{Re}[I_+(k)] . \quad (3.19)$$

IV. ZORBAS WAVE OPERATOR

As mentioned in the Introduction, it is known in the literature of the two-body Coulomb problem that matrix elements of the standard form of the T operator yield the correct scattering amplitude, but multiplied by a momentum-dependent term containing a phase factor that diverges as $\varepsilon\to 0$.[26] This phase factor also occurs in the present context. If the standard wave operators in Eqs. (2.5) are applied to a plane wave $\Psi_0(\mathbf{k},\mathbf{r})$, then

$$\Omega^{(\pm)}\Psi_0=\Gamma(1\mp i\eta)\left[\frac{2k^2}{\varepsilon}\right]^{\pm i\eta}\Psi^{(\pm)}(\mathbf{k},\mathbf{r}) , \quad (4.1)$$

where $\Psi^{(\pm)}$ is defined in Eq. (3.4). This identity can be verified explicitly in the same vein as results presented in the Appendix, although we do not do so here. We see that the correct wave function is thus obtained except for a multiplicative factor. This factor can, of course, be included in the wave operator, which is then in the form derived by Zorbas,[9]

$$\Omega_Z^{(\pm)}=\frac{1}{\Gamma(1\pm i\eta)}\left[\frac{\varepsilon}{2k^2}\right]^{\pm i\eta}\frac{(\pm i\varepsilon)}{E\pm i\varepsilon-H} . \quad (4.2)$$

Zorbas has also given the generalization of this operator to the case of N charged fragments.

This wave operator carries over directly to an expansion in partial waves, in which case we have

$$\Omega_{lZ}^{(\pm)}=\frac{1}{\Gamma(1\pm i\eta)}\left[\frac{\varepsilon}{2k^2}\right]^{\pm i\eta}\frac{(\pm i\varepsilon)}{E\pm i\varepsilon-h_l} . \quad (4.3)$$

It appears from Eq. (4.3) that there is no simple expedient for expressing this operator strictly in terms of the variable $E\pm i\varepsilon$, which would allow computations analogous to our earlier work.[1] However, certain identities derived there are of interest in the present investigation. Specifically, it was proven that, if we denote the p-wave radial resolvent with $E+i\varepsilon$ by $g^{(+)}$, then

$$i\varepsilon g^{(+)}f_{0\pm}=(1+g^{(+)}V)f_{0\pm}\mp f_+/J_+ . \quad (4.4)$$

In other words, although the two standard forms of the wave operator produce the same result when acting upon the spherical Riccati-Bessel function that is regular at the origin, they produce different results when acting upon the two irregular functions. The inhomogeneous terms f_+/J_+ cancel when the two spherical waves f_{0+} and f_{0-} are combined to give $\psi_0^{(+)}$ since

$$\psi_0=-\tfrac{1}{2}(f_{0+}+f_{0-}) . \quad (4.5)$$

Equation (4.4) is valid even in the Coulomb case, as is possible to verify directly through use of known forms of the radial Coulomb Green's function.[27] It was also conjectured that

$$i\varepsilon g^{(+)}f_{0+}=0 , \quad (4.6)$$

based on a proof for the analogous s-wave result.[1] Accepting Eq. (4.6) for the moment, Eqs. (4.4) and (4.6) tell us that

$$(1+g^{(+)}V)f_{0+}=f_+/J_+ . \quad (4.7)$$

Furthermore, the radial analog of Eq. (4.1),

$$i\varepsilon g^{(+)}\psi_0=\Gamma(1+i\eta)(2k^2/\varepsilon)^{i\eta}\psi^{(+)} , \quad (4.8)$$

combines with Eqs. (4.5) and (4.6) to yield

$$i\varepsilon g^{(+)}f_{0-}=-2\Gamma(1+i\eta)(2k^2/\varepsilon)^{i\eta}\psi^{(+)} . \quad (4.9)$$

Finally, this and Eq. (4.4) lead to

$$(1+g^{(+)}V)f_{0-}=-2\Gamma(1+i\eta)(2k^2/\varepsilon)^{i\eta}\psi^{(+)}-f_+/J_+ . \quad (4.10)$$

With these developments, we have the extremely interesting fact that the application of $1+g^{(+)}V$ to f_{0+} produces a function which is well-behaved in the limit $\varepsilon\to 0$. Application of $1+g^{(+)}V$ to f_{0-}, however, produces both terms that are well-behaved and terms that are not. The validity of analogous results in the s-wave case has been explicitly verified analytically. For the p wave, we instead turned directly to numerical verification. The techniques discussed in Sec. II were accordingly applied to the individual free-particle spherical waves. Defining the amplitudes

$$I_\pm(k)=\langle R_{1s}\,|\,r(1+g^{(+)}V)\,|\,f_{0\pm}\rangle , \quad (4.11)$$

the terms involving the resolvent can be approximated by

$$\langle R_{1s}\,|\,rg^{(+)}V\,|\,f_{0\pm}\rangle$$
$$\cong\sum_{i=1}^{N}\frac{(R_{1s\theta}\,|\,re^{i\theta}\,|\,\chi_{i\theta})(\chi_{i\theta}\,|\,V_\theta\,|\,f_{0\pm\theta})}{E+i\varepsilon-E_{i\theta}} , \quad (4.12)$$

Here $R_{1s\theta}$ and $f_{0\pm\theta}$ are the rotated versions of the functions [cf. Eqs. (2.12) and (2.15)], and $E_{i\theta}$ and $\chi_{i\theta}$ are obtained by numerical diagonalization of the complex radial Hamiltonian in the Laguerre basis of order 4. Comparing Eqs. (4.7) and (4.11), the amplitude I_+ is seen to agree with the earlier definition in Eq. (3.18). The results obtained for I_+ are shown as a function of basis size in Table I. It is seen there that the calculated amplitude is converging to the correct value, but at a fairly slow rate.

It is possible that faster convergence could be obtained by a careful optimization of the parameters λ and θ, but this was not investigated. Instead, an extrapolation procedure which previously proved successful was adopted.[1]

TABLE I. Values of the amplitude $I_+(k)=\langle R_{1s}\,|\,r\,|\,f_+\rangle/J_+$ calculated by use of $\Omega^{(+)}=1+G^{(+)}V$ and coordinate rotation. Extrapolated values refer to use of the epsilon algorithm on the intermediate sum in Eq. (4.13). Parameters used are $\lambda=1.8$, $\theta=0.18$, $Z=1$, and $k=1$. The exact $I_+(k)$ is $-2.617\,179\,23-i\,1.735\,619\,95$.

N	Calculated $I_+(k)$	Extrapolated $I_+(k)$
10	$-2.032\,064\,37-i\,1.398\,925\,44$	$-2.617\,051\,06-i\,1.735\,732\,35$
20	$-2.492\,073\,21-i\,1.886\,849\,68$	$-2.617\,179\,27-i\,1.735\,619\,96$
30	$-2.655\,939\,32-i\,1.761\,497\,77$	$-2.617\,179\,23-i\,1.735\,619\,95$
40	$-2.620\,834\,85-i\,1.726\,257\,69$	$-2.617\,179\,23-i\,1.735\,619\,95$
50	$-2.615\,087\,98-i\,1.735\,459\,66$	$-2.617\,179\,23-i\,1.735\,619\,95$
60	$-2.617\,201\,15-i\,1.735\,619\,45$	$-2.617\,179\,23-i\,1.735\,619\,95$

Inserting a resolution of the identity in terms of the Laguerre basis into Eq. (4.12), we have

$$\langle R_{1s}\,|\,rg^{(+)}V\,|\,f_{0\pm}\rangle \cong \sum_{n=0}\left[\sum_{i=1}^{N}\frac{(R_{1s\theta}\,|\,re^{i\theta}\,|\,\chi_{i\theta})(\chi_{i\theta}\,|\,\Phi_n)}{E+i\varepsilon-E_{i\theta}}\right](\Phi_n\,|\,f_{0\pm\theta})\,. \tag{4.13}$$

A sequence of partial sums is generated by successively taking the sum over n up to $0,1,2,\ldots,N-1$. These partial sums can be extrapolated by the epsilon algorithm, which is used to form pointwise Padé approximants from a given Taylor series.[25] The results are given in the extrapolated column of Table I, and show convincingly that the complex-coordinate method is performing very well at recovering the amplitude I_+. Similar efforts with I_- failed to shown any evidence of convergence, either with or without the extrapolation procedure. This confirms Eq. (4.4) and following. The partial amplitude lacking the phase factor is computationally quite stable, while the amplitude containing this factor is not.

It was mentioned in Eq. (3.18) that the full amplitude $I(k)$ could be obtained from the partial amplitude $I_+(k)$ if only there were an independent means of calculating the Jost function to the same accuracy. The Jost function is, of course, exactly known in the two-body problem, but this is of little help for extension to three or more particles.

The use of the operator $\Omega_{lZ}^{(+)}$ off the energy shell, that is, for a finite value of ε, is well-defined. Using the appropriate form of the radial Coulomb Green's function, we have been able to calculate analytically the result of applying the Zorbas wave operator with a finite value of ε to a free-particle wave function. (Actually, the calculation was for the s wave, but this does not matter.) Attempts to numerically analytically continue[28] the resulting amplitude back to the real axis were only accurate to within a few per cent, which is in no way comparable to the accuracy shown in Table I. This appears to be due to the fact that the off-shell amplitude near the real axis is a sum of two different series in the variable ε. The dominant series for small ε has a multiplicative phase factor involving ε. The off-shell amplitude can be multiplied by the inverse of this phase factor and the analytic continuation procedure applied to the result. It then turns out that the second series, even though vanishing for $\varepsilon\to 0$, causes interference in the extrapolation. Exactly this phenomenon has been discussed in the context of Coulomb T-matrix calculations by McCartor and Nuttall.[23] Similar difficulties in extrapolating $e^{\pm}$-H amplitudes have been discussed by Nuttall.[29]

V. TIME-INDEPENDENT FORMS OF THE DOLLARD WAVE OPERATOR

It was first shown by Dollard[5] that the wave operators for charged-particle interactions must be modified to account for the fact that the effects of Coulomb forces extend out to infinite separation. Working within the framework of time-dependent scattering theory, he obtained, instead of Eq. (2.2),

$$\Omega_D^{(\pm)}=s-\lim_{t\to\mp\infty}e^{iHt}e^{-iH_{0C}(t)}\,, \tag{5.1}$$

where $H_{0C}(t)$ is given by

$$H_{0C}(t)=H_0 t-Z\,\mathrm{sgn}(t)(-\nabla^2)^{-1/2}\ln(-2\,|\,t\,|\,\nabla^2)\,. \tag{5.2}$$

This operator has recently been used in finite-basis calculations of the Coulomb scattering amplitude by Kroger.[30] His work is in a certain sense a time-dependent analog of ours.

A transcription of Dollard's work to the time-independent framework has been given by Gibson and Chandler.[8] From their work, it is found that $\Omega_D^{(\pm)}$ may be expressed in similar fashion to Eq. (2.4),

$$\Omega_{GC}^{(\pm)}=\frac{\varepsilon^{\gamma}}{\Gamma(\gamma)}\int_0^{\infty}dt\,t^{\gamma-1}e^{-\varepsilon t}e^{\mp iHt}e^{\pm iH_{0C}(t)}\,. \tag{5.3}$$

Besides the presence of $H_{0C}(t)$ instead of $H_0 t$, Eq. (5.3) also differs from Eq. (2.4) by the parameter γ. This is positive real, but otherwise unrestricted. Related developments[31] may be found in the works of Prugovecki and Zorbas,[7] Tip,[11] and Gesztesy.[12]

Upon application of $\Omega_D^{(\pm)}$ to the plane wave state $|\,\mathbf{k}\rangle$, one obtains[11]

$$\Omega_{GC}^{(\pm)}|\mathbf{k}\rangle=\frac{\varepsilon^{\gamma}}{\Gamma(\gamma)}\int_0^{\infty}dt\,t^{\gamma-1}e^{-\varepsilon t}e^{\mp iHt}e^{\pm ik^2t/2\mp i\eta\ln(2k^2t)}|\mathbf{k}\rangle$$
$$=\frac{\varepsilon^{\gamma}}{\Gamma(\gamma)}(2k^2)^{\mp i\eta}\int_0^{\infty}dt\,t^{\nu-1}e^{\mp it(H-E\mp i\varepsilon)}|\mathbf{k}\rangle$$
$$=i^{\pm\nu}(2k^2)^{\mp i\eta}\varepsilon^{\gamma}\frac{\Gamma(\nu)}{\Gamma(\gamma)}(E\pm i\varepsilon-H)^{-\nu}|\mathbf{k}\rangle\ , \quad (5.4)$$

where we have used Eq. (3.5) and the definition

$$\nu=\gamma\mp i\eta\ . \quad (5.5)$$

Thus, the Gibson-Chandler form of the wave operator involves a complex power of the resolvent rather than the usual real power found in Eq. (2.5). As with the Zorbas operator, these results extend to multiparticle Coulomb problems with more than two charged fragments—a necessary feature for the possibility of extending our calculational methods to the three-body breakup in H^-. In proving that this leads to the correct Rutherford scattering cross section, Gibson and Chandler use the fact that this complex power of the resolvent can be replaced by a convolution integral over the energy appearing in the usual resolvent,

$$(E\pm i\varepsilon-H)^{-\nu}=\frac{i^{\pm(1-\nu)}}{\Gamma(\nu)\Gamma(1-\nu)}\times\int_0^{\infty}dy\,y^{-\nu}(E\pm iy\pm i\varepsilon-H)^{-1}\ ,$$
$$0<\gamma<1\ . \quad (5.6)$$

We have used this fact and Hostler's integral representation for the Coulomb Green's function[27] to verify that application of $\Omega_{GC}^{(+)}$ to Ψ_0 does indeed produce $\Psi^{(+)}$ of Eq. (3.4). As mentioned earlier, there is also a straightforward radial analog to these equations in which the wave operator contains the radial resolvent instead of the three-dimensional one,

$$\Omega_{lGC}^{(\pm)}=i^{\pm\nu}(2k^2)^{\mp i\eta}\varepsilon^{\gamma}\frac{\Gamma(\nu)}{\Gamma(\gamma)}(E\pm i\varepsilon-h_l)^{-\nu}\ . \quad (5.7)$$

We have used derivations along the lines of the Appendix to verify that the radial equation

$$\psi^{(\pm)}(k,r)=\Omega_{1,GC}^{(\pm)}\psi_0(k,r) \quad (5.8)$$

holds as well, but these results are not discussed here.

The key point in the use of $\Omega_{GC}^{(\pm)}$ would seem to be that the problems associated with the phase factor $\varepsilon^{\mp i\eta}$ are avoided when the complex power of the resolvent is used. We therefore used the matrix methods described before to construct the amplitude $I(k)$ according to

$$I(k)=\langle R_{1s}|\,r\Omega_{1,GC}^{(+)}|\,\psi_0\rangle\ . \quad (5.9)$$

We now take advantage of the freedom of choice for the specific value of γ. Using $\gamma=1$ and the free-particle wave equation satisfied by ψ_0, we get

$$\Omega_{1,GC}^{(+)}\psi_0=i\varepsilon(2ik^2)^{-i\eta}\Gamma(1-i\eta)(E+i\varepsilon-h)^{-1+i\eta}\psi_0$$
$$=\frac{\Gamma(1-i\eta)}{(2ik^2)^{i\eta}}[(E+i\varepsilon-h)^{i\eta}$$
$$+(E+i\varepsilon-h)^{-1+i\eta}V]\psi_0\ . \quad (5.10)$$

This puts the wave operator into a form suitable for taking the $\varepsilon\to0$ limit, since it only appears within the combination $E+i\varepsilon$, as discussed above for the standard wave operators of Eqs. (2.5).

The results of the above procedure are exemplified by the second column in Table II. The amplitudes obtained with varying basis size are clearly in the proximity of the exact amplitude, but there does not appear to be a systematic approach to the latter, and they eventually diverge as N is increased with all of the other parameters fixed. This is in distinction to the behavior (at least the observed behavior) for the shorter-range potentials considered in Ref. 1. It is, however, consistent with the general pattern of the results obtained by Kroger[30] in using Dollard's wave operator, upon which $\Omega_{GC}^{(\pm)}$ is based, for calculating the two-body scattering amplitude. We have found a very sharp dependence of our results upon the rotation angle θ and, to a lesser extent, the nonlinear parameter λ. In fact, it is very easy to enter into a parameter regime in which the calculated $I(k)$ diverges quite strongly with basis size. Attempts at extrapolating an intermediate sum as in the case of Eq. (4.13) met with no success.

With this disappointing turn, we attempted another procedure which recently proved successful in extracting

TABLE II. Values of $I(k)$ from Eq. (5.9) with Gibson-Chandler wave operator. The parameters used are the same as in Table I. Extrapolated values in this case are the $[N/2-1, N/2-1]$ approximants obtained from the sequence of calculated $I(k)$ for basis sizes $1,2,\ldots,N$. Exact $I(k)=0.652\,965\,5-i\,0.343\,065\,8$. Shown in the fourth column is the extrapolated total photoabsorption cross section, for which the exact value is 0.033 26 a.u.^{2}. The extrapolated value for the Coulomb phase shift $\delta_c=\arg[\Gamma(2+i\eta)]$ is given in the last column; the exact value is 0.4838 rad.

N	Calculated $I(k)$	Extrapolated $I(k)$	Extrapolated σ (a.u.^{2})	Extrapolated δ_c (rad)
10	$0.7024-i0.2463$	$0.7296-i0.2567$	0.036 57	0.3518
20	$0.6973-i0.2781$	$0.6842-i0.2943$	0.033 91	0.4062
30	$0.6846-i0.2927$	$0.6725-i0.3186$	0.033 85	0.4424
40	$0.6824-i0.3012$	$0.6662-i0.3281$	0.033 71	0.4576
50	$0.6714-i0.3017$	$0.6607-i0.3317$	0.033 41	0.4653
60	$0.6737-i0.3302$	$0.6608-i0.3324$	0.033 45	0.4661
70	$0.7135-i0.2661$	$0.6591-i0.3339$	0.033 37	0.4689
80	$0.4399-i0.3255$	$0.6592-i0.3341$	0.033 39	0.4691

free-free transition matrix elements for an asymptotic r^{-4} potential.[32] Although the complex-coordinate calculations in that case actually diverged with increasing basis size, it happened that Padé approximants (Shanks extrapolants) formed from the divergent sequence converged with no difficulty at all. The results of such a procedure in the present context are presented in the third column of Table II. The entries are the diagonal Padé approximants of order $N/2-1$ obtained from the amplitudes $I(k)$ calculated with basis sizes 1 to N. It appears from these and more extensive results that the extrapolation procedure converges with moderate stability with respect to the parameters used. However, if it does indeed converge, it is at such a slow rate that there is little promise in pursuing this route. The photoabsorption cross section σ and the Coulomb phase shift are both obtainable from the extrapolated results, the first through Eq. (3.17) and the second from the negative of the argument of the matrix element $I(k)$ (see Ref. 1). These quantities are also given in Table II.

With the failure of these results, we decided to investigate more carefully the limit $\varepsilon\to 0$. The hope was that, while the algorithm did not possess any obvious singular behavior in this limit, greater stability might still be achieved by moving off the energy shell, i.e., using a finite value of ε. This is dramatically borne out by the sample results in Table III, which show a marked improvement in the convergence of $I(k)$ with increasing ε. We therefore have a clear indication that the amplitudes can be calculated by the present procedure to a satisfactory accuracy, but that the quantities the calculations represent have a problematical behavior in the approach to the real axis. Furthermore, efforts at analytic continuation[28] of converged off-shell calculations back to the real axis met with only partial success, just as for $\Omega_Z^{(\pm)}$ in Sec. IV. This is at least consistent with the remarks made in the Appendix that the singularity structure in the analytic treatment of the two operators is the same.

It should be noted that ε in Table III has been taken to be zero. Finite values of ε obviate the need for complex-coordinate rotation in the resolvent matrix elements since the poles in the energy denominators are then bounded away from the real axis automatically. In addition to being *unnecessary*, however, nonzero values of θ were found to very quickly *degrade* the convergence of the finite ε amplitudes. This was something of a surprise since one expects (or hopes for) a certain degree of θ invariance in the matrix elements, especially given the damping influence of the bound-state wave function. The initial implication was that complex coordinates can fail miserably in some imprecisely known manner, and that this might contribute to the problems in the $i\varepsilon$ limit. Upon closer examination, however, the finite ε results were found to diverge in a spiralling manner as the basis size N was increased. Exactly this behavior was observed in the computation of free-free transition amplitudes for the long-range $-1/r^4$ potential of Ref. 32. We have found that the Padé extrapolation of the amplitudes with N which proved successful there also cures the divergence of the present off-shell amplitudes for nonzero θ. Thus, at least in conjunction with the extrapolation, a good degree of θ invariance is actually found. This is an informative discovery: Even if it is not immediately clear how the extrapolation could be generalized in more complex problems (e.g., multichannel problems or different bases lacking the analytic structure of the Laguerre functions), we have a clear indication that coordinate rotation does not irreversibly upset the convergence.

VI. MULHERIN-ZINNES WAVE OPERATOR

The third form of the Coulomb wave operator investigated here is the one obtained by Mulherin and Zinnes.[6] This operator, unlike the two above, is most naturally described in parabolic coordinates in the two-body case.[3] Application of the Mulherin-Zinnes wave operator to a plane wave yields the result

$$\Omega_{MZ}^{(\pm)}e^{i\mathbf{k}\cdot\mathbf{r}}=s-\lim_{t\to\mp\infty}e^{it(H-k^2/2)}\phi_c^{(\pm)}(\mathbf{k},\mathbf{r})\ , \tag{6.1}$$

where $\phi_C^{(\pm)}(\mathbf{k},\mathbf{r})$ is a plane wave modified by the familiar logarithmic distortion

$$\phi_C^{(\pm)}(\mathbf{k},\mathbf{r})=\exp[i\mathbf{k}\cdot\mathbf{r}\mp i\eta\ln(kr\mp\mathbf{k}\cdot\mathbf{r})]\ . \tag{6.2}$$

In analogy to non-Coulombic scattering, the form of Eq. (6.1) leads to a representation of the wave operator in terms of the resolvent

$$\Omega_{MZ}^{(\pm)}=\pm\frac{i\varepsilon}{E\pm i\varepsilon-H}(kr\mp\mathbf{k}\cdot\mathbf{r})^{\mp i\eta}\ . \tag{6.3}$$

This type of representation (at least for the two-body

TABLE III. Calculated values of the amplitude $I(k)$ for three values of ε in the Gibson-Chandler wave operator. The parameters used are the same as in Table I except that the angle θ is taken as zero.

N	$\varepsilon=0.0$	$\varepsilon=0.1$	$\varepsilon=0.2$
10	$0.14+i\,0.17$	$1.164\,03-i\,0.092\,77$	$1.490\,616\,1-i\,0.188\,501\,4$
20	$1.22-i\,0.63$	$1.254\,62-i\,0.234\,16$	$1.507\,954\,1-i\,0.208\,999\,4$
30	$0.69-i\,0.09$	$1.268\,28-i\,0.228\,89$	$1.509\,860\,0-i\,0.209\,580\,8$
40	$0.12+i\,1.10$	$1.268\,43-i\,0.225\,86$	$1.509\,976\,2-i\,0.209\,408\,4$
50	$0.46-i\,0.46$	$1.267\,70-i\,0.226\,87$	$1.509\,975\,4-i\,0.209\,411\,2$
60	$-0.14-i\,0.16$	$1.268\,20-i\,0.227\,10$	$1.509\,978\,1-i\,0.209\,410\,4$
70	$0.00+i\,0.47$	$1.268\,24-i\,0.226\,99$	$1.509\,978\,0-i\,0.209\,409\,5$
80	$0.23-i\,0.46$	$1.268\,22-i\,0.227\,01$	$1.509\,978\,0-i\,0.209\,409\,5$

problem) as been discussed briefly by Mulherin and Zinnes,[6] Chandler and Gibson,[21] and Rosenberg.[20]

It is apparent from Eq. (6.3) that the wave operator does not have as simple a form in spherical coordinates as in parabolic coordinates. Nonetheless, it is possible to project out the individual partial waves of the full scattering function as given in Eq. (2.8). If the z axis is taken in the $\mathbf{k}$ direction, then multiplication of Eq. (2.8) by $Y_{l0}^*(\hat{\mathbf{r}})$ and integration over the angles of $\mathbf{r}$ leads to

$$\psi_l^{(+)}=i^{-l}\pi kr\left[\frac{2}{2l+1}\right]^{1/2}\int d\hat{\mathbf{r}}\,\Psi^{(\pm)}(\mathbf{k},\mathbf{r})Y_{l0}^*(\hat{\mathbf{r}})\ . \tag{6.4}$$

The partial wave expansion of the full Green's function

$$G(\mathbf{r},\mathbf{r}';E\pm i\varepsilon)=\frac{1}{rr'}\sum_{l,m}g_l(r,r';E\pm i\varepsilon)Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{r}}') \tag{6.5}$$

can then be used to rewrite Eq. (6.4) as

$$\begin{aligned}\psi_l^{(\pm)}(k,r)&=i^{-l}\pi kr\left[\frac{2}{2l+1}\right]^{1/2}\int d\hat{\mathbf{r}}\,Y_{l0}^*(\hat{\mathbf{r}})\Omega_{MZ}^{(\pm)}\Psi_0(\mathbf{k},\mathbf{r})\\&=\pm\frac{i\varepsilon k}{2i^l}[\pi(2l+1)]^{-1/2}\int d\mathbf{r}'\frac{1}{r'}\,g_l(r,r';E\pm i\varepsilon)Y_{l0}^*(\hat{\mathbf{r}}')\phi_C^{(\pm)}(\mathbf{k},\mathbf{r}')\ .\end{aligned} \tag{6.6}$$

The integrals over angles in Eq. (6.6) can be performed without great difficulty. We have verified Eq. (6.6) explicitly using the radial Green's function, although we again pass over details.

Having convinced ourselves of the correctness of Eq. (6.6), we next turned to the problem of converting $\Omega_{MZ}^{(\pm)}$ to a form amenable to the previously described matrix methods. This can be accomplished by noting that $\phi_C^{(\pm)}(\mathbf{k},\mathbf{r})$ obeys the equation

$$(H-E)\phi_C^{(\pm)}=\frac{Z^2}{kr(kr\mp\mathbf{k}\cdot\mathbf{r})}\phi_C^{(\pm)}\ . \tag{6.7}$$

Thus, the full scattering function can be obtained by use of

$$\begin{aligned}\Psi^{(\pm)}(\mathbf{k},\mathbf{r})&=\Omega_{MZ}^{(\pm)}\Psi_0(\mathbf{k},\mathbf{r})\\&=\pm i\varepsilon G(E\pm i\varepsilon)\phi_C^{(\pm)}\\&=\left[1+G(E\pm i\varepsilon)\frac{Z^2}{kr(kr\mp\mathbf{k}\cdot\mathbf{r})}\right]\phi_C^{(\pm)}\ .\end{aligned} \tag{6.8}$$

This has a similar structure to the ordinary results described by Eq. (2.4) except that the plane wave is replaced by the distorted plane wave $\phi_C^{(\pm)}$ and V to the right of the resolvent is replaced by a term which decays as $1/r^2$. It is also singular in the forward (backward) direction, but all integrals will still be finite.

The radial wave function can now be obtained through the projection procedure and use of the new form of the Mulherin-Zinnes wave operator[22]

$$\begin{aligned}\psi^{(+)}(k,r)&=(\tfrac{2}{3})^{1/2}\frac{\pi kr}{i}\int d\hat{\mathbf{r}}\,Y_{l0}^*(\hat{\mathbf{r}})\Psi^{(+)}(\mathbf{k},\mathbf{r})\\&=\psi_B^{(+)}(k,r)+\psi_R^{(+)}(k,r)\ .\end{aligned} \tag{6.9}$$

A natural division of $\psi^{(+)}(k,r)$ has been made here into a Born-like term and a residual term. The Born term is the p-wave projection of the asymptotic wave function $\phi_C^{(+)}$, and the residual term makes up the difference between it and the exact p-wave function. The angular integrals can be done exactly, with the results

$$\psi_B^{(+)}(k,r)=\frac{ikr}{1-i\eta}(2kr)^{-i\eta}e^{-ikr}\left[{}_1F_1(1;2-i\eta;2ikr)-\frac{2}{2-i\eta}\,{}_1F_1(2;3-i\eta;2ikr)\right]\ , \tag{6.10}$$

$$\begin{aligned}\psi_R^{(+)}(k,r)&=(3\pi)^{-1/2}\frac{Z^2}{2i}\int_0^\infty dr'\,g(r,r';E+i\varepsilon)\int d\hat{\mathbf{r}}'[(kr'-\mathbf{k}\cdot\mathbf{r}')^{-1}Y_{l0}^*(\hat{\mathbf{r}}')\phi_C^{(+)}(\mathbf{k},\mathbf{r}')]\\&=\frac{Z}{2}(2k)^{-i\eta}\int_0^\infty dr'\,g(r,r';E+i\varepsilon)(r')^{-1-i\eta}e^{-ikr'}\left[\frac{2}{1-i\eta}\,{}_1F_1(2;2-i\eta;2ikr')-{}_1F_1(1;1-i\eta;2ikr')\right]\ .\end{aligned} \tag{6.11}$$

The radial amplitude $I(k)$ now consists of two contributions, with the one originating from $\psi_B^{(+)}$ posing no computational problems. The one arising from $\psi_R^{(+)}$ can be calculated by the complex-coordinate method again, with the Green's function approximated by the L^2 methods used before.

Table IV lists some representative findings from this approach. The amplitudes calculated with $\Omega_{MZ}^{(+)}$ are stable for some range of N and then eventually diverge quickly. This problem can be largely overcome by introducing a resolution of the identity to the right of $g^{(+)}$ and then using the epsilon algorithm to extrapolate the resulting sum

TABLE IV. Calculated values of $I(k)$ using Mulherin-Zinnes wave operator. Extrapolated values in this case refer to intermediate-sum extrapolation similar to that used in Table I. Parameters used are $\lambda=0.8$, $\theta=0.6$, $Z=1$, and $k=1$. Exact $I(k)=0.652\,965\,5-i\,0.343\,065\,8$. Shown in the fourth column is the extrapolated total photoabsorption cross section, for which the exact value is 0.033 26 a.u.^{2}. The extrapolated value for the Coulomb phase shift is given in the last column; the exact value is 0.4838 rad.

N	Calculated $I(k)$	Extrapolated $I(k)$	Extrapolated σ (a.u.^{2})	Extrapolated δ_c (rad)
10	$0.6403-i\,0.3017$	$0.6644-i\,0.2464$	0.030 70	0.3551
20	$0.6523-i\,0.3172$	$0.6537-i\,0.3212$	0.032 43	0.4567
30	$0.6533-i\,0.3263$	$0.6541-i\,0.3348$	0.033 01	0.4731
40	$0.6532-i\,0.3306$	$0.6525-i\,0.3392$	0.033 06	0.4794
50	$0.6532-i\,0.3332$	$0.6530-i\,0.3381$	0.033 06	0.4778
60	$0.6836-i\,0.3257$	$0.6531-i\,0.3389$	0.033 10	0.4787
70	$9.5-i\,13.9$	$0.6531-i\,0.3385$	0.033 08	0.4782
80	$1\times10^5-i\,2.2\times10^6$	$0.6527-i\,0.3385$	0.033 05	0.4784

[cf. Eq. (4.13)]. As can be seen from the extrapolated column of Table IV, this procedure remains stable even in the face of rampant divergence of the original amplitudes. We have generally found that the Mulherin-Zinnes operator is capable of greater accuracy than the Gibson-Chandler operator. This is represented by comparison of the phases δ_c obtained here and in Table II. We attribute this increase in precision to the $1/r^2$ behavior of the factor to the right of the resolvent in Eq. (6.8). This is still considerably less accurate than desired, if implementation in the three-body case is to be attempted. Once again, evaluation at finite ε stabilizes the amplitude very strongly.

VII. DISCUSSION

An extensive investigation has been made into use of finite-basis and wave-operator techniques to calculate the hydrogenic photoionization amplitude. Different means of calculating the matrix element replete with the phase information contained in the scattering function have been attempted, but have been met with only qualified success. The quality of amplitudes obtained suggests utility of the method in molecular photoionization. However, numerical difficulties have been encountered which appear to be connected with the nonanalytic structure for Coulomb scattering in the $\varepsilon\to0$ limit. The difficulties have limited the ultimate precision to about 1%. This is discouraging given that similar methods have reproduced total photoeffect cross sections to several significant figures[18,33] and that equally good convergence was obtained in the use of only the outgoing spherical wave in Sec. IV. On the positive side, it is hoped that the evidence presented here will eventually lead to a resolution of the convergence problems, and allow the methods used to be extended to multiple ionization processes.

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APPENDIX

Gibson and Chandler[8] have given a rigorous momentum-space demonstration that the wave operator in Eq. (5.4) leads to the correct form of the two-body Coulomb scattering amplitude. This derivation moreover was free of divergent phases that had existed in previous calculations. We give below a sketch of the coordinate-space proof that $\Omega_{GC}^{(+)}$ transforms a plane wave into the appropriate Coulomb continuum function $\Psi^{(+)}$ given in Eq. (3.4). The outline of the integral evaluation (which involves taking a tricky singular limit similar to that in Ref. 8) is informative because it is closely related to those occurring for the other forms of the wave operator, and also in the partial-wave analogs for the Gibson-Chandler and Zorbas cases. We have confidence that the details of rigor can be filled in, but they are not our primary concern in this paper.

Equations (5.4) and (5.6) lead immediately to the following expression for the Coulomb scattering function:

$$\Psi^{(+)}(\mathbf{k},\mathbf{r})=\frac{i(2k^2)^{-i\eta}\varepsilon^{1+i\eta}}{\Gamma(\gamma)\Gamma(1-\nu)}\times\int_0^\infty dy\,y^{-\nu}\int d\mathbf{r}'\,G(\mathbf{r},\mathbf{r}';E+iy+i\varepsilon)\times\Psi_0(\mathbf{k},\mathbf{r}')\,. \tag{A1}$$

From Hostler's work,[27] there is a convenient integral representation for G:

$$G(\mathbf{r},\mathbf{r}';E+iy+i\varepsilon)$$
$$=\frac{iK}{2\pi}\int_1^\infty ds\left[\left(\frac{s+1}{s-1}\right)^{i\mu}e^{iKs(r+r')}\times J_0(2K[rr'(s^2-1)]^{1/2}\cos(\theta/2))\right], \tag{A2}$$

where J_0 is a Bessel function and

$$\tfrac{1}{2}K^2=E+iy+i\varepsilon\ ,\quad \mathrm{Im}(K)>0\ , \tag{A3}$$

$$\mu=\frac{Z}{K}\ , \tag{A4}$$

$$\cos\theta=\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'\ . \tag{A5}$$

To allow for certain values of μ, the integral can be transformed into a contour integral which encircles the point $s=1$ with an infinitesimal radius.

We now have for Eq. (A1), using the results of Ref. 27,

$$\Psi^{(+)}=-\frac{2(2k^2)^{-i\eta}\varepsilon^{1+i\eta}}{(2\pi)^{3/2}\Gamma(\gamma)\Gamma(1-\nu)}\int_0^\infty dy\,y^{-\nu}K\int_1^\infty ds\left[\left(\frac{s+1}{s-1}\right)^{i\mu}(K^2s^2-k^2)^{-3}\times[-2iKs(K^2s^2-k^2)+2K^3\mathbf{k}\cdot\mathbf{r}s(s^2-1)-(K^2s^2+k^2)K^2(s^2-1)r]\times\exp\left[iKsr\frac{K^2-k^2}{K^2s^2-k^2}+i\mathbf{k}\cdot\mathbf{r}\frac{K^2(s^2-1)}{K^2s^2-k^2}\right]\right]. \tag{A6}$$

With hindsight, we may identify the term

$$(K^2s^2-k^2)^{-3}=[k^2(s^2-1)+i(y+\varepsilon)]^{-3} \tag{A7}$$

as the cause of the divergence of the double integral in Eq. (A6). If ε were taken to be 0 before the integral evaluations, then there would be a nonintegrable singularity at $s=1$ and $y=0$. This is integrable as long as ε is finite, but the result will be ill-behaved as $\varepsilon\to 0$. To extract the singularity explicitly, therefore, we can make the changes of variables,

$$s=1+2\varepsilon v\ , \tag{A8}$$

$$y=\varepsilon x\ , \tag{A9}$$

Retaining everywhere only the leading powers of ε, we find that Eq. (A6) becomes

$$\Psi^{(+)}=-\frac{4k^4(2k^2)^{-i\eta}e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}\Gamma(\gamma)\Gamma(1-\nu)}\int_0^\infty dx\,x^{-\nu}\int_0^\infty dv\left\{\frac{v^{-i\eta}}{[2k^2v+i(x+1)]^3}\left[-i\left[v+\frac{i(x+1)}{2k^2}\right]-v(kr-\mathbf{k}\cdot\mathbf{r})\right]\times\exp\left[-\frac{(x+1)(kr-\mathbf{k}\cdot\mathbf{r})}{2k^2v+i(x+1)}\right]\right\}. \tag{A10}$$

While this looks very complicated still, it is possible to simplify it enormously by making another change of variables,

$$v=\frac{i(x+1)}{2k^2}w\ , \tag{A11}$$

followed by a rotation of the integration path back to the real axis. We thus find that the integral becomes

$$\Psi^{(+)}=\frac{i^{-i\eta}e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}\Gamma(\gamma)\Gamma(1-\nu)}\left[\int_0^\infty dx\,x^{-\nu}(x+1)^{-1-i\eta}\right]\times\left[\int_0^\infty dw\,w^{-i\eta}(w+1)^{-2}\left[1-\frac{iw(kr-\mathbf{k}\cdot\mathbf{r})}{w+1}\right]\exp\left[\frac{i(kr-\mathbf{k}\cdot\mathbf{r})}{w+1}\right]\right], \tag{A12}$$

which can be evaluated from known integrals,

$$\Psi^{(+)}=\frac{e^{\eta\pi/2}e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}\Gamma(\gamma)\Gamma(1-\nu)}\frac{\Gamma(\gamma)\Gamma(1-\nu)}{\Gamma(1+i\eta)}\left[|\Gamma(1+i\eta)|^2\,{}_1F_1(i\eta;1;i(kr-\mathbf{k}\cdot\mathbf{r}))\right]$$
$$=\frac{e^{\eta\pi/2}}{(2\pi)^{3/2}}\Gamma(1-i\eta)e^{i\mathbf{k}\cdot\mathbf{r}}\,{}_1F_1(i\eta;1;i(kr-\mathbf{k}\cdot\mathbf{r}))\ . \tag{A13}$$

Thus, the exact three-dimensional Coulomb wave function has been recovered, assuring us of the proper normalization in our numerical calculations and reaffirming the correctness of the results of Gibson and Chandler.

It should be noted especially that, in the final analysis, the y or x dependence of the integral has factored; that is, the variable associated with the convolution over the energy of the normal resolvent was only involved in the most singular part of the integral by a multiplicative (normalization) factor. Upon reflection, this fact shows that the Coulomb wave function could be obtained by the use of the ordinary Coulomb resolvent given a suitable normalizing factor. This, of course, is precisely what is accomplished by the Zorbas wave operator.[9]

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