

Computation of Elastic Scattering Phase Shifts via Analytic Continuation of Fredholm Determinants Constructed Using an L^2 Basis

W. P. Reinhardt, D. W. Oxtoby, and T. N. Rescigno*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 30 December 1971)

It is shown that the Fredholm determinant for the Lippmann-Schwinger equation may be computed for complex energies using only L^2 basis functions. Analytic continuation to the real axis in the $E + i\epsilon$ limit gives elastic scattering phase shifts over a continuous range of energies, showing that it is not necessary to explicitly enforce asymptotic boundary conditions for numerical scattering computations, and suggesting that elastic electron-atom or -ion scattering information may be obtained using standard bound-state configuration-interaction methods.

Numerical solutions of nonrelativistic potential-scattering problems usually proceed by construction of an approximate solution of the Schrödinger equation which satisfies an appropriate asymptotic boundary condition. In a recent review¹ Burke and Seaton have remarked that enforcing this asymptotic boundary condition leads to many of the problems which make scattering solutions more difficult to obtain than the corresponding bound-state solutions. Schlessinger and co-workers² and McDonald and Nuttall³ have avoided the difficulties inherent in the usual asymptotic form of the wave function by computation of partially off-shell T -matrix elements for complex values of the momentum k , so that the wave function decreases exponentially, allowing the use of bound-state computational techniques; scattering information is obtained by analytic continuation to real k . In another approach, Hazi and co-workers^{4,5} have shown that scattering information at physical resonance energies can be extracted from computations carried out entirely in a L^2 basis, suggesting that explicit enforcement of the asymptotic boundary condition is not essential. It is the purpose of this Letter to show that these seemingly diverse methods can be combined to give a prescription for computation of the Fredholm determinant at complex energies using only square-integrable basis functions. As the computational procedure does not depend on a particular physical (real) value of the energy, numerical analytic continuation of the determinant to the real axis gives elastic scattering information over a continuous range of energies for a large class of local and nonlocal potentials including those of the form r^{-q} ($q \geq 1$) as $r \rightarrow \infty$, for which completely off-shell T -matrix methods fail. The numerical results presented imply that explicit enforcement of the correct asymptotic form of the wave function is not necessary for numerical scatter-

ing computations and that standard bound-state computational techniques may be used directly for numerical solution of scattering problems, no new types of matrix elements being required. The partial-wave Fredholm determinant^{6,7}

$$D(z) = \det \left(\frac{z - H}{z - H^0} \right) = \det [1 - G^0(z)V], \quad (1)$$

where $H = H^0 + V$ and $G^0(z) = (z - H^0)^{-1}$, is analytic in the cut E plane for a wide class of potentials⁸; knowledge of the determinant gives the elastic phase shift $\delta(E)$ through the well-known relation⁶

$$D(E + i\epsilon) = |D(E + i\epsilon)| e^{-i\delta(E)}.$$

Simple diagonalization of H and H^0 in an N -term L^2 basis set $\{\varphi_i\}$ formally gives

$$D^{\text{approx}}(z) = \prod_{i=1}^N [(z - E_i)/(z - E_i^0)], \quad (2)$$

where E_i and E_i^0 are "eigenvalues" of H and H^0 , respectively.⁹ The approximation of Eq. (2) is real for E on the real axis, having a series of poles rather than a branch cut along the positive real axis. Equation (2) thus does not directly give useful information for positive real values of z . On the other hand, if in a region of the complex z plane $D^{\text{approx}}(z)$ is a good approximation to $D(z)$, we can use Eq. (2) to compute the determinant in this region, and then analytically continue to take the $E + i\epsilon$ limit¹⁰ in order to extract physical scattering information. That this is a practical and accurate procedure is shown by the following numerical results.

Table I shows s -wave phase shifts for the problem of electron-hydrogen-atom scattering in the static approximation as a function of the number of L^2 functions in the expansion basis. In this case the expansion functions were the first N generalized Laguerre polynomials¹¹ $L_n^2(\alpha r)$ which are orthogonal on the interval $(0, \infty)$ with the

TABLE I. Convergence of s -wave phase shifts for electron-hydrogen atom scattering in the stable approximation as a function of N , the number of Laguerre polynomials used.

k	$N=5$	$N=10$	$N=20^a$	$N=30$	Exact ^b
0.1	0.7153	0.7182	0.7224	0.7222	0.7222
0.2	0.9283	0.9659	0.9726	0.9726	0.9725
0.6	1.024	1.022	1.021	1.021	1.021
1.0	0.9290	0.9078	0.9063	0.9059	0.9055
5.0	0.3642	0.4322	0.4379	0.4364	0.4338

^aThe optimum continuations were found to be approximately $[\frac{1}{2}N, \frac{1}{2}N]$, where N is the number of basis functions. The results in the table are [2, 2], [4, 4], [8, 8], and [10, 10] continuations, respectively.

^bThe exact results were obtained using the method of Ref. 7.

weight function $r^{2\alpha}e^{-\alpha r}$; α was chosen to be 3.75 but the results were not sensitive to this choice for $1 \leq \alpha \leq 3.75$. $D^{\text{approx}}(z)$ was continued to the real axis using the point-wise rational-fraction technique² used by Schlessinger. The rational fraction

$$R_{[n,n]}(z) = \left(\sum_{i=0}^n P_i z^i \right) / \left(1 + \sum_{i=1}^n q_i z^i \right), \quad (3)$$

was fitted to $D^{\text{approx}}(z)$ at $2n+1$ points in the complex plane, uniquely determining the coefficients p_i and q_i . In actual computations a continued-fraction¹² representation of $R_{[n,n]}(z)$ was used, avoiding the actual construction of the p_i and q_i . The phase of $R_{[n,n]}(E+i\epsilon)$ for real E gives the scattering phase shifts over a continuous range of energies. Table II shows the convergence of

the phase shift as a function of the choice of continuation points for a computation using ten basis functions [$N=10$ in Eq. (2)]; the results are stable to about 1% for moderate size continuations. For $N=20$, a similar convergence study shows stabilization to about 0.2% over the range $k=0.1$ to 1.0 a.u. Table III shows results for p - and d -wave scattering of electrons from the static hydrogen potential and s -wave scattering of a particle from a square well and a repulsive Coulomb square well. Computations with a centrifugal barrier¹³ or Coulomb potential simply require that the appropriately modified H^0 be used; for example

$$H^0 = \frac{p^2}{2m} + \frac{l(l+1)}{2r^2} \pm \frac{z}{r}$$

for l -wave Coulomb scattering. The fact that L^2 basis functions are used means that the necessary integrals over long-range potentials cause no difficulty and no new types of matrix elements are needed for Coulomb or higher partial-wave computations.

A more rigorous discussion of the convergence of the L^2 expansion can probably be based on consideration of the convergence properties of $\text{tr}\{[G^A(z)V]^N\}$ and $\text{tr}|G^A(z)V|$ in the complex z plane, where $G^A(z)V$ is an L^2 expansion of $G^0(z)V$. Convergence of these traces is a sufficient condition for convergence of the standard expansion of $\det[1 - G^0(z)V]$ in the complex plane.

In summary, bound-state eigenvalue techniques may be used to construct approximations to the Fredholm determinant for complex energy. Point-wise rational-fraction analytic continuation

TABLE II. Dependence of phase shift on n , the order of the continuation, for s -wave static phase shift and a basis set of ten Laguerre polynomials.

k	Exact	[1, 1] ^a	[3, 3] ^a	[4, 4] ^a	[4, 4] ^b	[4, 4] ^c	[6, 6] ^a	[14, 14] ^d
0.1	0.7222	0.6957	0.7011	0.7182	0.7278	0.7201	0.6994	0.1452
0.2	0.9725	0.9955	0.9657	0.9659	0.9716	0.9711	0.9602	0.8634
0.6	1.021	1.052	1.024	1.022	1.022	1.023	1.024	-0.1362
1.0	0.9055	0.8994	0.9066	0.9078	0.9079	0.9074	0.9074	0.0147
5.0	0.4338	0.2681	0.4260	0.4322	0.4436	0.4382	0.4318	-0.112

^aThe $2n+1$ input points were chosen as follows: $\text{Re}(k_i)$ spaced at intervals of 0.1, starting at 0.1; $\text{Im}(k_i) = \min[2\text{Re}(k_i), 1.0]$.

^b $\text{Re}(k_i)$ twice as large as in footnote a above, spreading out the points.

^c $\text{Im}(k_i)$ twice as large as in footnote a above, moving input points farther from the real axis.

^dThese nonconvergent results are expected; as N increases the continuation begins to represent actually the ratio of polynomials of Eq. (2) and thus contains no scattering information; in fact, for the present example, if continuation of order [10, 10] and above were performed exactly the phase shifts would be identically zero.

TABLE III. Computations of the $l=1$ and $l=2$ phase shifts, δ_1^{stat} and δ_2^{stat} , for the scattering of electrons from hydrogen in the static approximation, s -wave phase shifts δ^{sw} for scattering from a square well,^{a,b} and the s -wave Coulomb phase shift^a δ^{swC} {relative to $\arg[\Gamma(1+i/k)]$ } for scattering from a square well plus a repulsive Coulomb potential.^c Exact results are shown in parentheses.

k	δ_1^{stat}	δ_2^{stat}	δ^{sw}	δ^{swC}
0.2	0.0021 (0.0021)	0.000 04 (0.000 02)	0.2330 (0.1986)	0.0028 (3×10^{-12})
0.4	0.0146 (0.0146)	0.0006 (0.0005)	0.4100 (0.3905)	0.0017 (1.8×10^{-5})
0.6	0.0405 (0.0405)	0.0030 (0.0029)	0.5972 (0.5934)	0.0029 (0.0030)
0.8	0.0752 (0.0751)	0.0087 (0.0087)	0.7884 (0.7884)	0.0351 (0.0337)
1.0	0.1116 (0.1115)	0.0179 (0.0178)	0.9802 (0.9812)	0.1236 (0.1260)
1.2	0.1448	0.0297	1.1706 (1.1710)	0.2779 (0.2788)
1.4	0.1726	0.0428	1.3775 (1.3575)	0.4718 (0.4706)

^aThe static results were computed with a fifty-term Laguerre basis, the square-well and Coulomb square-well results with thirty harmonic-oscillator functions.

^bThe (attractive) square-well parameters are depth 20 a.u. and width 1.0 a.u.

^cA unit repulsive Coulomb potential was added to the square well discussed in footnote b above.

then allows extraction of the elastic phase shifts over a continuous range of real energies. The method is easily applied in the presence of singular, long-range, local, or nonlocal potentials and suggests that elastic electron scattering information may be obtained from standard atomic or molecular configuration-interaction programs where the complete L^2 basis would be the usual Slater or Gaussian functions.

Terry Murtaugh's work on the convergence of the continuations has greatly aided the present authors. One of the authors (W.P.R.) acknowledges many conversations with A. U. Hazi and H. S. Taylor; had their stabilization calculations (Refs. 4 and 5) not been successful, the present computations might not have been attempted. A grant from the duPont Young Faculty Fund made the computational work possible, and is gratefully acknowledged.

*National Science Foundation Predoctoral Fellow (1969-1972).

¹P. G. Burke and M. S. Seaton, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1971), Vol. 10, p. 1. This volume contains an up-to-date review of current methods for construction of scattering information by solving the Schrödinger equation and inspecting its asymptotic form.

²L. Schlessinger and C. Schwartz, *Phys. Rev. Lett.* **16**, 1173 (1966); L. Schlessinger, *Phys. Rev.* **168**, 1411

(1968), and **171**, 1523 (1968); R. W. Haymaker and L. Schlessinger, in *The Padé Approximant in Theoretical Physics*, edited by G. A. Baker and J. L. Gammel (Academic, New York, 1970), Chap. 11.

³F. A. McDonald and J. Nuttall, *Phys. Rev. Lett.* **23**, 361 (1969), and *Phys. Rev. A* **4**, 1821 (1971).

⁴A. U. Hazi and H. S. Taylor, *Phys. Rev. A* **2**, 1109 (1970).

⁵A. U. Hazi and M. Fels, *Chem. Phys. Lett.* **8**, 582 (1971); M. Fels and A. U. Hazi, *Phys. Rev. A* **4**, 662 (1971).

⁶See, for example, M. Baker, *Ann. Phys. (New York)* **4**, 27 (1958).

⁷W. P. Reinhardt and A. Szabo, *Phys. Rev. A* **1**, 1162 (1970).

⁸For a large class of local potentials, $D(z)$ is the Jost function; see, for example, R. G. Newton, *The Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966), Chap. 12.

⁹By "eigenvalues" we mean the N eigenvalues of the matrices H and H^0 formed by projection of H and H^0 onto the N functions chosen to be in the basis set.

¹⁰The limiting procedure has been successfully carried out in the context of a standard Fredholm (Ref. 7) computation: T. S. Murtaugh and W. P. Reinhardt, *Chem. Phys. Lett.* **11**, 562 (1971).

¹¹*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. GPO, Washington, D. C., 1964), Chap. 22.

¹²H. S. Wall, *The Analytic Theory of Continued Fractions* (Van Nostrand, Princeton, N. J., 1948).

¹³T. N. Rescigno and W. P. Reinhardt, *J. Phys. B: Proc. Phys. Soc.*, London **4**, 1279 (1971), give a related procedure in terms of a spherical Bessel function expansion.