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S-Matrix Method for the Numerical Determination of Bound States

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A rapid numerical technique for the determination of bound states of a partial-wave-projected Schrödinger equation is presented. First, one needs to integrate the equation only outwards as in the scattering case, and second, the number of trials on κ^2 $(=-E)$ necessary to determine the eigenenergy and the corresponding eigenfunction is considerably less than in the usual method. As a nontrivial example of the technique, bound states are calculated in the exchange approximation for the e^--He^+ system and $l=1$ partial wave.

I. INTRODUCTION

In the case of scattering from centrally symmetric potentials, one solves a projected Schrödinger equation for a particular partial wave for a continuous range of energy E $(=k^2)$. For any value of k a scattering solution of the Schrödinger equation is obtained by choosing the boundary conditions on $\Psi_l(r)$ and its derivative at origin and integrating the equation outwards. At asymptotic distances the required solutions are oscillating functions of the distance r. The bound states occur at negative energies $(E=-\kappa^2)$ and for the bound state values of κ the solutions of the Schrödinger equation are square-integrable and thus at asymptotic distances are of the form $e^{-\kappa r}$. For a value of κ not corresponding to a bound state, a solution of the Schrödinger equation has both the regular and the irregular solution mixed in, and at asymptotic distances the irregular part $(e^{\kappa r})$ dominates and thus the outward integration diverges. The usual method to get around this difficulty is to integrate the equation inwards and outwards and impose continuity at a midway point.[1] The inner and outer logarith-

mic derivatives of $\Psi_l(r)$ at a midway point "r" are plotted for a set of values of κ. The points where the two logarithmic derivative curves intersect correspond to bound states.

In this paper we present a direct and speedier method for the determination of bound states within any desired accuracy.[2] In this method, first, we need to integrate the equation only outwards, as in the scattering case. Second, the number of trials required on κ to determine the bound-state value within a desired accuracy are rapidly reduced to a few.

II. METHOD

The method is based on the analyticity properties of the S matrix in the complex k plane. It is well known[3] that poles of the S-matrix element $S_l(k)$ on the positive imaginary axis ($k = i\kappa$) correspond to bound states, when the analytic continuation of $S_l(k)$, away from the real k axis, exists. Bargmann[4] has shown that the S matrix is analytic within the strip (called the Bargmann strip) defined by $0 < |\mathrm{Im}k| < \frac{1}{2}\mu$ for potentials which satisfy

$$\int_0^\infty e^{\mu r} |V(r)|\, dr < \infty \ . \tag{1}$$

If the potential vanishes identically beyond a distance r_∞, then the Bargmann strip extends over the whole complex k plane. In potential theory the analyticity properties of $S_l(k)$ have been understood by studying the analyticity of the Jost functions $f_l(k, r)$ and $f_l(-k, r)$. From Eq. (2) to Eq. (6) below, we briefly summarize the defining relations and boundary conditions for the partial-wave-projected Schrödinger equation.

The solution of the partial-wave Schrödinger equation in terms of the Jost functions is written as

$$\Psi_l(k, r) = \frac{i}{2k^{l+1}} \left[f_l(-k) f_l(k, r) - (-1)^l f_l(k) f_l(-k, r) \right], \tag{2}$$

where $\Psi_l(k, r)$ satisfies the boundary conditions

$$\begin{aligned} &\Psi_l(k, 0) = 0 \ , \\ &\Psi_l'(k, 0) = \delta_{l0} \ . \end{aligned} \tag{3}$$

The Jost functions $f_l(k, r)$ and $f_l(-k, r)$ are two independent solutions of the partial-wave Schrödinger equation and asymptotically satisfy the boundary condition

$$e^{\pm ikr} f_l(\pm k, r) \underset{r\to\infty}{=} i^l \ , \tag{4}$$

with the Wronskian

$$\begin{aligned} &W[f_l(k, r), f_l(-k, r)] = (-1)^l 2ik \ , \\ &f_l(\pm k) = \lim_{r\to 0} \frac{(\pm kr)^l}{(2l-1)!!} f_l(\pm k, r) \ . \end{aligned} \tag{5}$$

For asymptotic distances Eq. (2) has the form

$$\Psi_l(k, r) \underset{r\to\infty}{=} C f_l(k) [S_l^{-1}(k)\, e^{-ikr} + (-1)^{l+1} e^{ikr}] \ . \tag{6}$$

For the continuation $k \to i\kappa$ within the Bargmann strip and for a value of κ close to one of the poles of $S(k)$ at $k = i\kappa_n$ ($n = 1, 2, 3, \ldots$, etc.), Eq. (6) takes the form

$$\Psi_l(i\kappa, r) = C f_l(i\kappa) [-A(\kappa - \kappa_n)\, e^{\kappa r} + (-1)^{l+1} e^{-\kappa r}] \ , \tag{7}$$

where A is a constant. At an asymptotic point r_∞ we form the function $p(r_\infty) \equiv \Psi_l(i\kappa, r_\infty)/e^{\kappa r_\infty}$, which happens to be

$$p(r_\infty) = C f_l(i\kappa) [-A(\kappa - \kappa_n) + (-1)^{l+1} e^{-2\kappa r_\infty}] \ . \tag{8}$$

One notices that $p(r_\infty)$ vanishes at the bound-state value κ_n with an error of the order of $|e^{-2\kappa_n r_\infty}|$. Thus, to determine the value of the κ_n within the above accuracy, one integrates the equation for a set of values of κ and plots $p(r_\infty)$ against κ. The points where $p(r_\infty)$ changes sign correspond to the bound states. It is obvious that one should be able to determine κ_n within any desired accuracy by selecting r_∞ appropriately and in just a few trials of κ. Also, one needs to integrate the equation only outwards.

It is likely that, at the points $k = i\kappa_n$, $f_l(i\kappa_n)$ may vanish, but in this case the wave function in Eq. (7) vanishes. These zeros are related to the redundant zeros of the S matrix and have been shown to exist in the case of the exponential potential by Ma.[5] But within the Bargmann strip $f_l(i\kappa_n)$ does not vanish if $f_l(-i\kappa_n)$ vanishes, because of the Wronskian relation (5). It is possible to avoid all questions about the redundant zeros if one assumes that the potential vanishes identically beyond a distance "r_∞," in which case the Bargmann strip extends over the whole complex k plane. In practice it is always possible to choose a distance r_∞ sufficiently large so that for all practical purposes $V(r)$ and $V(r)\theta(r_\infty - r)$ are equivalent.

III. CALCULATION AND RESULTS

As an illustration of the above method, we solve the $e^- + He^+$ scattering problem for $l = 1$ and get the

TABLE I. $^{1,3}P$ bound-state results and comparison with the results of Cohen and Kelly.

State	Calculated E_t (Ry)	Cohen and Kelly[a]
$^1P(1)$	−4.24490	−4.24490
$^1P(2)$	−4.10946	−4.10948
$^1P(3)$	−4.06061	−4.06180
$^3P(1)$	−4.26236	−4.26264
$^3P(2)$	−4.11516	−4.11516
$^3P(3)$	−4.06338	−4.06424

[a]Reference 6.

energies of the lowest three singlet and three triplet P bound states of He. The wave function of the system including exchange is given by

$$\Psi_l(\vec{r}_1, \vec{r}_2) = \frac{u_l(r_1)}{r_1}\ Y_{l0}(\Omega_1)\ \phi_0(r_2) \pm 1 \rightleftharpoons 2\ , \qquad (9)$$

where $u_l(r_1)$ is the scattering function and $\phi_0(r_2)$ is the ground-state wave function of He^+,

$$\phi_0(r_2) = \left(\frac{z^3}{\pi}\right)^{1/2} e^{-zr_2}\ . \qquad (10)$$

The function $u_l(r)$ is obtained by solving the integro-differential equation

$$\left(\frac{d^2}{dr^2} + k^2 + v(r) - \frac{l(l+1)}{r^2}\right) u_l(r) \pm 4z^3 e^{-zr}\left[(k^2+z^2)\ \delta_{l0}\ r\int_0^\infty e^{-zr_2}\ r_2 u_l(r_2)\, dr_2 - \frac{2}{(2l+1)}\left(r^{-l}\int_0^r e^{-zr_2}\ r_2^{l+1}\ u_l(r_2)\, dr_2 + r^{l+1}\int_r^\infty e^{-zr_2}\ r_2^{-l}\ u_l(r_2)\, dr_2\right)\right] = 0\ , \qquad (11)$$

where

$$v(r) = \frac{2(z-1)}{r} + 2[z + (1/r)]e^{-2zr} \qquad (12)$$

and z is the charge of the nucleus. We also have total energy $E_t = -z^2 + k^2$. For calculating the bound-state energy, we solve the above equation for $k^2 = -\kappa^2$ and study the function

$$p(r_\infty) = \frac{u_l(r_\infty)}{e^{\kappa r_\infty}}\ . \qquad (13)$$

We choose $r_\infty = 40.00$, and study the singlet case first.

With a mesh size of 0.002 in κ^2, we find $p(r_\infty) = -0.1476\times10^{-4}$ at $\kappa^2 = 0.244$ and $p(r_\infty) = +0.1832\times10^{-4}$ at $\kappa^2 = 0.246$. If we look at the two values of $p(r_\infty)$ and guess a linear interpolation, one is led to search for a value of κ^2 about midway between 0.2440 and 0.2460. Thus, employing a mesh size of 0.00001 and searching around 0.2450, we find $-0.4726\times10^{-7} < p(r_\infty) < 0.2275\times10^{-6}$ for $0.24490 < \kappa^2 < 0.24491$. This shows that the first bound state is at $E_t = -4.24490$ Ry. In Table I we present our results for the lowest three singlet and three triplet P states. We compare our results with those of Cohen and Kelly,[6] and the agreement is seen to be satisfactory. If r_∞ is increased to 60.00, our results are exactly the same as those of Ref. 6. It is to be emphasized that the exchange approximation used in this calculation is a restricted approximation and therefore the presently calculated results have not been compared with the accurate results of Schiff *et al.*,[7] who include effectively all correlations between the electrons.

We find that in this method the position of the bound states is at first located by choosing a rough mesh size in κ^2, and then by using a finer mesh size in the neighborhood of the location one may improve the value to within a desired accuracy. This results in desirable computational economy.

In conclusion, this method should be particularly good to calculate the quantum defects of highly excited levels, as the energies of these closely spaced states can be obtained by this method.

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