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Numerical Solution of Scattering Equations with Nonlocal Potentials

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A noniterative method, first communicated by Marriott, for solving the integro-differential equations which arise in electron–atom scattering theory, is developed for a general class of nonlocal potentials for both coupled and uncoupled equations. Algorithms are given for the numerical solution in the uncoupled case using Simpson's rule for the quadrature scheme. As a sample calculation e^{-}-He elastic scattering phase shifts are calculated using the static-exchange approximation with a renormalized density matrix. Hartree–Fock phase shifts are tabulated for He and Ne and compared to previous calculations.

1. INTRODUCTION

When calculating the scattering properties of atomic systems it is often necessary to solve integral equations of the type

$$u(x) = R(x) + \int_0^\infty \int_0^\infty K_0(x, y)\, \Sigma(y, z)\, u(z)\, dy\, dz, \tag{1}$$

where $K_0(x, y)$ is a Green's function of a second order differential operator and the nonlocal potential Σ has the form,

$$\Sigma(y, z) = V(y)\, \delta(y - z) + \begin{cases} \sum_{n=1}^{N} \alpha_n(y)\, \beta_n(z), & y < z, \\ \sum_{n=1}^{N} \mu_n(y)\, \nu_n(z), & y > z. \end{cases} \tag{2}$$

A noniterative method, first communicated by Marriot [1], makes it possible to build up $u(x)$ by a few simple outward integrations. The method has been successfully applied to a variety of problems [1–4] using both the differential and integral forms of Eq. (1). The purpose of this paper is to present in concise notation the solution of Eq. (1) when Σ has the form in Eq. (2) along with efficient algorithms

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for its numerical evaluation. In Section 4 the solution is generalized to the case of coupled equations. As a sample calculation the elastic scattering phase shifts for the e^--He system are calculated in the static exchange approximation using both the Hartree–Fock and the renormalized density matrix. HF phase shifts for Ne are also presented.

2. Formal Solution

Let $R(x)$ and $I(x)$ be solutions of

$$H_{op} \begin{Bmatrix} R(x) \\ I(x) \end{Bmatrix} = 0, \tag{3}$$

which are regular and irregular, respectively, at the origin, and let $K_0(x, y)$ be a Green's function for the second order differential operator H_{op}, i.e.,

$$H_{op} K_0(x, y) = \delta(x - y). \tag{4}$$

Then K_0 can be expressed as

$$K_0(x, y) = \begin{cases} R(x)\, I(y), & x < y, \\ I(x)\, R(y), & x > y. \end{cases} \tag{5}$$

Since K_0 and Σ are known functions the integration on y is done first in Eq. (1). If the function $K(x, y)$ is defined by

$$K(x, z) = \int_0^\infty K_0(x, y)\, \Sigma(y, z)\, dy,$$

then using Eqs. (2) and (5) we obtain

$$\begin{aligned} K(x, z) &= R(x)\, I(z)\, V(z) + I(x) \sum_{n=1}^{N} \beta_n(z) \int_0^x R(y)\, \alpha_n(y)\, dy \\ &\quad + R(x) \sum_{n=1}^{N} \beta_n(z) \int_x^z I(y)\, \alpha_n(y)\, dy \\ &\quad + R(x) \sum_{n=1}^{N} \nu_n(z) \int_z^\infty I(y)\, \mu_n(y)\, dy \qquad (x < z) \\ &= I(x)\, R(z)\, V(z) + I(x) \sum_{n=1}^{N} \beta_n(z) \int_0^z R(y)\, \alpha_n(y)\, dy \\ &\quad + I(x) \sum_{n=1}^{N} \nu_n(z) \int_z^x R(y)\, \mu_n(y)\, dy \\ &\quad + R(x) \sum_{n=1}^{N} \nu_n(z) \int_x^\infty I(y)\, \mu_n(y)\, dy \qquad (x > z). \end{aligned} \tag{6}$$

If we define the auxiliary functions

$$f_n^1(x) = \int_0^x R(y)\,\alpha_n(y)\,dy, \tag{7a}$$

$$f_n^2(x) = \int_0^x I(y)\,\alpha_n(y)\,dy, \tag{7b}$$

$$f_n^3(x) = \int_0^x R(y)\,\mu_n(y)\,dy, \tag{7c}$$

$$f_n^4(x) = \int_x^\infty I(y)\,\mu_n(y)\,dy, \tag{7d}$$

then Eq. (6) can be written as

$$\begin{aligned} K(x, z) &= R(x) \left\{ I(z)\,V(z) + \sum_{n=1}^{N} \beta_n(z) f_n^2(z) + \sum_{n=1}^{N} \nu_n(z) f_n^4(z) \right\} \\ &\quad + \sum_{n=1}^{N} \beta_n(z) \{ I(x) f_n^1(x) - R(x) f_n^2(x) \} \qquad (x < z) \\ &= I(x) \left\{ R(z)\,V(z) + \sum_{n=1}^{N} \beta_n(z) f_n^1(z) - \sum_{n=1}^{N} \nu_n(z) f_n^3(z) \right\} \\ &\quad + \sum_{n=1}^{N} \nu_n(z) \{ I(x) f_n^3(x) + R(x) f_n^4(x) \} \qquad (x > z). \end{aligned} \tag{8}$$

$K(x, z)$ now has the simple form

$$K(x, z) = \begin{cases} \sum_{n=0}^{N} a_n(x)\, b_n(z), & x < z, \\ \sum_{n=0}^{N} c_n(x)\, d_n(z), & x > z, \end{cases} \tag{9}$$

if we define

$$\begin{aligned} a_0(x) &= R(x), \\ b_0(x) &= I(x)\,V(x) + \sum_{n=1}^{N} \{\beta_n(x) f_n^2(x) + \nu_n(x) f_n^4(x)\}, \\ c_0(x) &= I(x), \\ d_0(x) &= R(x)\,V(x) + \sum_{n=1}^{N} \{\beta_n(x) f_n^1(x) - \nu_n(x) f_n^3(x)\}, \\ &\left.\begin{aligned} a_n(x) &= I(x) f_n^1(x) - R(x) f_n^2(x), \\ b_n(x) &= \beta_n(x), \\ c_n(x) &= I(x) f_n^3(x) + R(x) f_n^4(x), \\ d_n(x) &= \nu_n(x). \end{aligned}\right\} n \neq 0 \end{aligned} \tag{10}$$

Equation (1) has the form

$$u(x) = R(x) + \int_0^\infty K(x, z)\, u(z)\, dz \tag{11}$$

and can be evaluated on a grid of points using Marriot's method straightforwardly.

3. Algorithms

In this section the details of Marriot's method will be developed using Simpson's rule for the quadrature scheme along with efficient algorithms for programming each step.

Referring to the kernel of Eq. (9) define the integral operator G by

$$Gu(x) = \sum_{n=0}^{N} c_n(x) \int_0^x d_n(y)\, u(y)\, dy - \sum_{n=0}^{N} a_n(x) \int_0^x b_n(y)\, u(y)\, dy. \tag{12}$$

Equation (11) then reads

$$(1 - G)\, u(x) = \sum_{n=0}^{N} A_n a_n(x) \tag{13}$$

with

$$A_n = \delta_{n0} + \int_0^\infty b_n(y)\, u(y)\, dy. \tag{14}$$

The solution $u(x)$ can be expressed as a linear combination of elementary solutions, i.e., if

$$(1 - G)\, u_n(x) = a_n(x), \tag{15}$$

then

$$u(x) = \sum_{n=0}^{N} A_n u_n(x). \tag{16}$$

The unknown constants A_n can be found algebraically from the solutions of Eq. (15). That is, if

$$B_{nm} = \int_0^\infty b_n(y)\, u_m(y)\, dy, \tag{17}$$

then

$$(\mathbf{I} - \mathbf{B})\mathbf{A} = \mathbf{\Delta}, \tag{18}$$

where $\mathbf{\Delta}$ is the first column of the unit matrix $\mathbf{I}$. Equation (18) is a standard problem for which a program can be found in the IBM supplied Scientific Subroutine

Package. The asymptotic form of $u(x)$ for large x is also needed for the evaluation of the scattering phase shifts. From Eqs. (9) and (11) this can be seen to be

$$\lim_{x\to\infty} u(x) = R(x) + \sum_{n=0}^{N} c_n(x) \int_0^\infty d_n(y)\, u(y)\, dy. \tag{19}$$

When the functions $V(x)$, $\beta_n(x)$, and $\nu_n(x)$ are exponentially decaying, as they are for scattering from neutral atoms, Eq. (19) becomes

$$\lim_{x\to\infty} u(x) = R(x) + I(x) \left\{ \int_0^\infty d_0(y)\, u(y)\, dy + \sum_{n=1}^{N} f_n{}^3(\infty) \int_0^\infty d_n(y)\, u(y)\, dy \right\}. \tag{20}$$

The tangent of the phase shift will be proportional to the constant in Eq. (20), i.e.,

$$\tan\delta \sim \sum_{n,m=0}^{N} F_n{}^3 D_{nm} A_m\,, \tag{21}$$

where

$$F_n{}^3 = \begin{cases} 1, & n = 0, \\ f_n{}^3(\infty), & n \neq 0, \end{cases} \tag{22}$$

and

$$D_{nm} = \int_0^\infty d_n(y)\, u_m(y)\, dy. \tag{23}$$

The central problem then is building up the solutions of Eq. (15) by an outward integration. First, the x-axis is divided into grids, as shown in Fig. 1, with the increment, Δ_i of each grid being twice that of the previous grid. Letting $u_m(k) \equiv u_m(x_i + k\Delta_i)$ on a given grid, then using Simpson's rule Eq. (15) becomes

$$\begin{aligned} u_m(k) = a_m(k) &+ \sum_{n=0}^{N} \{c_n(k)\, D_{nm}(k-2) - a_n(k)\, B_{nm}(k-2)\} \\ &+ \Delta_i/3 \sum_{n=0}^{N} c_n(k)\{d_n(k-2)\, u_m(k-2) + 4d_n(k-1)\, u_m(k-1)\} \\ &- \Delta_i/3 \sum_{n=0}^{N} a_n(k)\{b_n(k-2)\, u_m(k-2) + 4b_n(k-1)\, u_m(k-1)\}, \end{aligned} \tag{24}$$

where

$$\begin{aligned} B_{nm}(k) &= \int_0^{x_i+k\Delta_i} b_n(y)\, u_m(y)\, dy \qquad (25) \\ &= B_{nm}(k-2) + \Delta_i/3\{b_n(k-2)u_m(k-2) + 4b_n(k-1)u_m(k-1) + b_n(k)u_m(k)\} \end{aligned}$$

and $D_{nm}(k)$ is defined analogously.

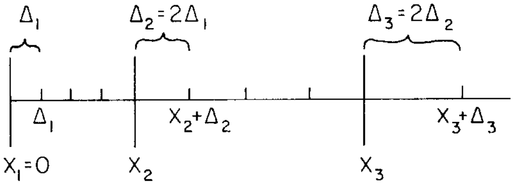

FIG. 1. Grid structure for numerical solution of Eq. (15) using Simpson's rule.

The functions a_n, b_n, c_n, and d_n are calculated in a separate step and stored sequentially in the order

$$\ldots a_0(k)\, a_1(k) \ldots a_N(k)\, c_0(k) \ldots c_N(k)\, b_0(k) \ldots b_N(k)\, d_0(k) \ldots d_N(k)\, a_0(k+1) \ldots .$$

Buffers are maintained for the functions a_n, b_n, c_n, d_n, u_n, B_{nm}, and D_{nm} evaluated at three consecutive points.

All the data for the point k is stored in the first buffer, for the point $k-1$ in the second buffer, and for the point $k-2$ in the third buffer. Then to calculate the functions $u_m(x)$ on a given grid the following sequence of events takes place for each point:

(1) The data from the second buffer is moved to the third buffer.

(2) The data from the first buffer (except for a_n and c_n) is moved to the second buffer.

(3) a_n, b_n, c_n, and d_n for the new point are read into their portion of the first buffer.

(4) Calculate the quantities,

$$\begin{aligned} S &= \sum_{n=0}^{N} \{c_n(k)\, d_n(k-2) - a_n(k)\, b_n(k-2)\}, \\ T &= \sum_{n=0}^{N} \{c_n(k)\, d_n(k-1) - a_n(k)\, b_n(k-1)\}. \end{aligned} \tag{26}$$

(5) For all m calculate the new u_m's with

$$\begin{aligned} u_m(k) = a_m(k) &+ (\Delta/3)\, S u_m(k-2) + (4\Delta/3)\, T u_m(k-1) \\ &+ \sum_{n=0}^{N} \{c_n(k)\, D_{nm}(k-2) - a_n(k)\, B_{nm}(k-2)\}. \end{aligned} \tag{27}$$

(6) For all m, n calculate the new B_{nm} and D_{nm}'s using Eq. (25).

(7) Store the $u_m(k)$'s on a sequential data set.

When the last point of the grid has been processed, the buffers are initialized for the next grid by moving the data from the third buffer into the second buffer. Processing then begins with (1) above.

At the end of the last grid the B_{nm} and D_{nm}'s in the first buffer provide the constants of Eqs. (17) and (23) to solve for the constants A_n and the phase shifts. The u_m's can then be read back one point at a time and the final solution u constructed.

Initializing the buffers for the first grid constitutes a special problem which must be treated carefully, since errors made here are carried through the rest of the calculations. $u_m(0)$, $B_{nm}(0)$, and $D_{nm}(0)$ are zero and $u_m(1)$, $B_{nm}(1)$, and $D_{nm}(1)$ are calculated using the trapezoid rule

$$u_m(1) = a_m(1), \tag{28a}$$

$$B_{nm}(1) = (\Delta_1/2)\{b_n(0)\, u_m(0) + b_n(1)\, u_m(1)\}, \tag{28b}$$

$$D_{nm}(1) = (\Delta_1/2)\{d_n(0)\, u_m(0) + d_n(1)\, u_m(1)\}. \tag{28c}$$

This, however, is not enough for initialization because the limits of $b_n(x)\, u_m(x)$ and $d_n(x)\, u_m(x)$ as x goes to zero are not always zero. Since they occur in Eqs. (28b) and (28c) and in Eqs. (24) and (25) for the point $k = 2$, they must be evaluated for each specific problem and read in. An interpolation scheme could be used here to avoid having to consider these limits for each special case.

Once the limiting values are obtained, Eqs. (28) are evaluated and stored in the second buffer. Equations (24) and (25) are evaluated for the point $k = 2$ and stored in the first buffer. Then processing begins with step (1) and continues until all grids and points have been processed.

The step which constructs the functions a_n, b_n, c_n, and d_n is specialized for the case $\alpha_n(x) = \nu_n(x)$, $\beta_n(x) = \mu_n(x)$ and assumes that the following data is stored sequentially:

$$\alpha_1(k)\, \alpha_2(k) \ldots \alpha_N(k)\, \beta_1(k) \ldots \beta_N(k)\, V(k)\, I(k)\, R(k)\, \alpha_1(k+1) \ldots . \tag{29}$$

Buffers are maintained which hold the above data as well as the functions f_n^1, f_n^2, f_n^3, and f_n^4 at three consecutive points. The function f_n^4 defined in Eq. (7d) diverges, in general, as x goes to zero. Therefore, it is evaluated using the formula

$$\begin{aligned} f_n^4(k) &= \int_{\Delta_1}^{\infty} I(y)\, \beta_n(y)\, dy - \int_{\Delta_1}^{x_i + k\Delta_i} I(y)\, \beta_n(y)\, dy \\ &= f_n^5(\infty) - f_n^5(k). \end{aligned} \tag{30}$$

Consequently, it is necessary to count through the points twice, once to construct f_n^1, f_n^2, f_n^3, and f_n^5 and once to construct f_n^4, a_n, b_n, c_n, and d_n. The data (29) for the points $k = 1$ and $k = 3$ for the first grid are for the points $\Delta_1/2$ and $3\Delta_1/2$, respectively. This is so the functions f_n^1, f_n^2, f_n^3, and f_n^5 can be initialized with Simpson's rule. Therefore, to initialize for the first grid, the data of (29) is read in for points $k = 1, 2$ and the f's calculated by

$$\begin{aligned} f_n^1(1) &= (\Delta_1/6)\{4R(1)\,\alpha_n(1) + R(2)\,\alpha_n(2)\}, \\ f_n^2(1) &= (\Delta_1/6)\{4I(1)\,\alpha_n(1) + I(2)\,\alpha_n(2)\}, \\ f_n^3(1) &= (\Delta_1/6)\{4R(1)\,\beta_n(1) + R(2)\,\beta_n(2)\}, \\ f_n^5(1) &= 0 \end{aligned} \tag{31}$$

and stored in the second buffer. Then the data for $k = 3, 4$ is read in and

$$f_n^1(2) = f_n^1(1) + (\Delta_1/6)\{R(2)\,\alpha_n(2) + 4R(3)\,\alpha_n(3) + R(4)\,\alpha_n(4)\} \tag{32}$$

is used with analogous expressions for f_n^2, f_n^3, and f_n^5, and they are stored in the first buffer. The f's are then calculated at the remaining points in a similar manner to the B_{nm}'s of Eq. (25). At each point the functions f_n^1, f_n^2, f_n^3, f_n^5, V, I, and R are written on a sequential data set. The second pass reads this data back, one point at a time, evaluates Eqs. (10) and stores them for the u_m construction routine.

4. Coupled Equations

The method is also applicable to sets of coupled equations. The solutions can be written analogously to those of Section 2 and will be presented here. However, the programs of Section 3 have not been generalized and no sample calculation is given.

The equations to be solved are

$$u_k(x) = R_k(x) + \sum_{l=1}^{N_c} \int_0^\infty \int_0^\infty K_k(x, y)\,\Sigma_{kl}(y, z)\,u_l(z)\,dy\,dz, \tag{33}$$

with the nonlocal potentials, and

$$\Sigma_{kl}(y, z) = V_{kl}(y)\,\delta(y - z) + \begin{cases} \sum_{m=1}^{N_{kl}} \alpha_{klm}(y)\,\beta_{klm}(z), & y < z, \\ \sum_{m=1}^{N_{kl}} \mu_{klm}(y)\,\nu_{klm}(z), & y > z. \end{cases} \tag{34}$$

The integration on y gives

$$\int_0^\infty K_k(x, y)\,\Sigma_{kl}(y, z)\,dy = \begin{cases} \sum_{m=0}^{N_{kl}} a_{klm}(x)\,b_{klm}(z), & x < z, \\ \sum_{m=0}^{N_{kl}} c_{klm}(x)\,d_{klm}(z), & x > z. \end{cases} \tag{35}$$

The definitions of a_{klm} , etc. are given by Eqs. (7) and (10) when n is replaced by klm, and $R(x)$ and $I(x)$ are replaced by $R_k(x)$ and $I_k(x)$, respectively, and V is replaced with V_{kl} .

Defining the integral operators G_{kl} by

$$G_{kl}u(x) = \sum_{m=0}^{N_{kl}} c_{klm}(x) \int_0^x d_{klm}(y)\, u(y)\, dy - \sum_{m=0}^{N_{kl}} a_{klm}(x) \int_0^x b_{klm}(y)\, u(y)\, dy \tag{36}$$

and the constants

$$A_{klm} = \delta_{kl}\delta_{m0} + \int_0^\infty b_{klm}(y)\, u_l(y)\, dy, \tag{37}$$

Eq. (33) becomes

$$u_k(x) = \sum_l G_{kl}u_l(x) + \sum_{l,m} A_{klm}a_{klm}(x), \tag{38}$$

where the relation

$$a_{kl0}(x) = R_k(x), \qquad \text{all } l, \tag{39}$$

has been used.

Again , the solutions u_k can be expressed in terms of solutions of a set of auxiliary equations

$$u^i_{klm}(x) = \sum_j G_{ij}u^j_{klm}(x) + \delta_{ik}a_{klm}(x). \tag{40}$$

These solutions can be built up numerically in a manner analogous to that described in Section 3. Multiplying both sides of Eq. (40) by A_{klm} and summing shows that the u_i's can be expressed as

$$u_i(x) = \sum_{k,l,m} A_{klm}u^i_{klm}(x). \tag{41}$$

Substituting (41) into (37) gives

$$A_{klm} = \delta_{kl}\delta_{m0} + \sum_{k',l',m'} B_{klm;k'l'm'}A_{k'l'm'} , \tag{42}$$

where

$$B_{klm;k'l'm'} = \int_0^\infty b_{klm}(y)\, u^l_{k'l'm'}(y)\, dy. \tag{43}$$

In matrix notation Eq. (42) is identical to Eq. (18)

$$(\mathbf{I} - \mathbf{B})\mathbf{A} = \mathbf{\Delta}, \tag{44}$$

where **A** and **Δ** are column vectors with the elements A_{klm} and $\delta_{kl}\delta_{m0}$, respectively. The dimensionality of the general problem is

$$N = \sum_{k,l=1}^{N_c} (N_{kl} + \delta_{kl}), \tag{45}$$

where N_c is the number of coupled equations. However, symmetries in the Σ_{kl} may reduce this number. For example, if $\alpha_{klm}(x) = \alpha_{kl'm'}(x)$ then $u^i_{klm}(x) = u^i_{kl'm'}(x)$ and the dimensionality is reduced by one.

5. Sample Calculation

As an example, the programs described in Section 3 have been used to calculate the s, p, and d phase shifts for the elastic scattering of electrons from neutral He atoms using a static-exchange approximation to the optical potential with a renormalized density matrix. Since the differences between the phase shifts from this approximation and the Hartree–Fock approximation represent a third order correction to the phase shifts which have recently been calculated by Yarlagadda *et. al.* [5] and Knowles and McDowell [6] it is of interest to have accurate values for them.

The scattering functions will be solutions of the equation

$$(\nabla^2 + k^2 - 2V)\,\Psi(\vec{x}) = 0, \tag{46}$$

where k^2 is the energy in Rydbergs of the scattered electron and V is defined by

$$V\Psi(\vec{x}) = -\frac{Z}{x}\Psi(\vec{x}) + 2\int \frac{\rho(\vec{y},\vec{y})}{|\vec{x}-\vec{y}|}\,d^3\vec{y}\;\Psi(\vec{x}) - \int \frac{\rho(\vec{x},\vec{y})}{|\vec{x}-\vec{y}|}\,\Psi(\vec{y})\,d^3\vec{y}. \tag{47}$$

The density matrix ρ is expressed in terms of the natural orbitals R_{il} and occupation numbers η_{il} as

$$\rho(\vec{x},\vec{y}) = \sum_{ilm} \eta_{il} R_{il}(x)\, R^*_{il}(y)\, Y_{lm}(\hat{x})\, Y^*_{lm}(\hat{y}). \tag{48}$$

The solution $\Psi(\vec{x})$ is expanded in spherical harmonics as

$$\Psi(\vec{x}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_l \frac{u_l(x)}{x}\, Y_{lm}(\hat{x}), \tag{49}$$

and the radial equation for the u_l's is

$$\left\{\frac{d^2}{dx^2} + k^2 - \frac{l(l+1)}{x^2}\right\} u_l(x) = 2V^{\text{local}}(x)\,u_l(x) - 2\int_0^\infty \Sigma_l(x,y)\,u_l(y)\,dy, \tag{50}$$

where

$$\begin{aligned} V^{\text{local}}(x) &= -\frac{Z}{x} + 2\int \frac{\rho(\vec{y}, \vec{y})}{|\vec{x} - \vec{y}|}\, d^3\vec{y} \\ &= 2\sum_{il} \eta_{il}(2l+1) \left\{ \int_x^\infty R_{il}^2(y)\, y\, dy - \frac{1}{x}\int_x^\infty R_{il}^2(y)\, y^2\, dy \right\} \end{aligned} \tag{51}$$

and

$$\Sigma_{l'}(x, y) = \sum_{il\lambda} \eta_{il}(2l+1) \begin{pmatrix} l' & l & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{cases} x^{\lambda+1} R_{il}(x)\, y^{-\lambda} R_{il}(y), & x < y, \\ x^{-\lambda} R_{il}(x)\, y^{\lambda+1} R_{il}(y), & x > y, \end{cases} \tag{52}$$

and $\left(\begin{smallmatrix} l' & l & \lambda \\ 0 & 0 & 0 \end{smallmatrix}\right)$ is a Wigner $3-j$ symbol.

This gives a nonlocal potential of the form of Eq. (2) with

$$V(y) = 2V^{\text{local}}(y), \tag{53a}$$

$$\alpha_n(x) = \nu_n(x) \equiv \alpha_{il\lambda}(x) = -2\eta_{il}(2l+1) \begin{pmatrix} l' & l & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 x^{\lambda+1} R_{il}(x), \tag{53b}$$

$$\beta_n(x) = \mu_n(x) \equiv \beta_{il\lambda}(x) = x^{-\lambda} R_{il}(x). \tag{53c}$$

The Green's function of Eq. (5) is defined by

$$R(x) = kxj_l(kx), \tag{54a}$$

$$I(x) = -xy_l(kx), \tag{54b}$$

where j_l and y_l are the spherical Bessel and Neumann functions, respectively, whose asymptotic behavior is

$$\begin{aligned} \lim_{z\to\infty} j_l(z) &= (1/z)\sin(z - l\pi/2), \\ \lim_{z\to\infty} y_l(z) &= (1/z)\cos(z - l\pi/2). \end{aligned} \tag{55}$$

Equations (53) and (54) were used to prepare the data for the programs of Section 3. The limiting values of $b_n(x)\, u_m(x)$ and $d_n(x)\, u_m(x)$ are all zero except for

$$\lim_{x\to 0} b_0(x)\, u_0(x) = \frac{2Z}{2l+1}, \tag{56}$$

where Z is the atomic number and l is the partial wave under consideration. With the definition (54b) the tangent of the phase shift is given by

$$\tan\delta = -(1/k) \sum_{n,m=0}^{N} F_n{}^3 D_{nm} A_m\,. \tag{57}$$

The density matrix of Eq. (48) is identical in form to the Hartree–Fock density matrix of closed shell atoms. Therefore, to test the programs, the HF phase shifts were calculated for Ne, and the results are compared to those of Thompson [7] in Table I. The occupied HF orbitals used were those of Clementi *et al.* [8]. The grid

TABLE I

Comparison of HF Phase Shifts for Electron Scattering from Ne with Those of Thompson [7]

	s-wave		*p*-wave		*d*-wave	
k	This work	Thompson	This work	Thompson	This work	Thompson
0.001	3.1405	—	3.1416	—	0.00000	—
0.01	3.1309	—	3.1416	—	0.00000	—
0.1	3.0350	—	3.1404	—	0.00000	—
0.2	2.9280	2.931	3.1324	—	0.00006	—
0.3	2.8205	2.824	3.1133	—	0.00038	—
0.4	2.7123	2.716	3.0818	—	0.00143	—
0.5	2.6038	2.607	3.0393	3.040	0.00394	0.004
0.6	2.4956	—	2.9882	—	0.00870	—
0.7	2.3881	—	2.9314	2.933	0.01652	—
0.8	2.2821	—	2.8714	2.873	0.02804	—
0.9	2.1781	—	2.8102	2.812	0.04365	—
1.0	2.0765	2.078	2.7495	2.751	0.06354	0.065
2.0	1.2354	—	2.2717	—	0.39898	—
3.0	0.6661	—	1.9977	—	0.65686	—

TABLE II

Structure of Grid Points Used to Numerically Evaluate Eq. (50)

Increment	No. of points	Length of grid
0.78125 (−3)	40	0.03125
0.15625 (−2)	40	0.06250
0.3125 (−2)	40	0.12500
0.6250 (−2)	40	0.25000
0.0125	40	0.50000
0.0250	40	1.0000
0.0500	40	2.0000
0.1000	80	8.0000
Totals	360	11.96875

Numbers in Parentheses are Powers of 10.
Columns 1 and 3 are in Units of Bohr Radii.

TABLE III

s, *p*, and *d* Phase Shifts for Electron Scattering from He

		s-Wave					*p*-Wave					*d*-Wave			
		HF density		Renormalized density		Polar. potential	HF density		Renormalized density		Polar. potential	HF density	Renormalized density		Polar. potential
E(eV)	k	[a]	[b]	[c]	[d]	[e]	[a]	[b]	[c]	[d]	[e]	[a]	[c]	[d]	[e]
0.14(−4)	0.001	3.1401	—	—	—	—	—	—	—	—	—	—	—	—	—
0.14(−2)	0.01	3.1268	—	—	—	—	—	—	—	—	—	—	—	—	—
0.1360	0.1	2.9937	—	2.9939	2.9939	3.0367	0.0004	—	—	0.0004	0.0094	—	—	—	—
0.5542	0.2	2.8475	—	—	—	—	0.0033	—	—	—	—	0.00001	—	—	—
1.224	0.3	2.7049	2.7048	—	—	—	0.0106	0.0105	—	—	—	0.00009	—	—	—
2.177	0.4	2.5672	2.5672	—	—	—	0.0236	0.0233	—	—	—	0.00034	—	—	—
3.401	0.5	2.4357	2.4356	2.4367	2.4371	2.4741	0.0425	0.0422	0.0428	0.0430	0.0806	0.00091	0.00093	0.00093	0.00533
4.898	0.6	2.3113	2.3111	—	—	—	0.0667	0.0663	—	—	—	0.00201	—	—	—
6.666	0.7	2.1943	2.1942	—	—	—	0.0946	0.0943	—	—	—	0.00376	—	—	—
8.707	0.8	2.0851	2.0850	—	—	—	0.1246	0.1243	—	—	—	0.00627	—	—	—
11.02	0.9	1.9838	—	—	—	—	0.1545	—	—	—	—	0.00957	—	—	—
13.60	1.0	1.8901	1.8900	1.8916	1.8923	1.9372	0.1831	0.1831	0.1837	0.1847	0.2510	0.01364	0.01375	0.01381	0.02819
30.61	1.5	1.5220	—	—	—	—	0.2843	—	—	—	—	0.04192	—	—	—
54.42	2.0	1.2789	—	1.2798	—	—	0.3267	—	0.3269	—	—	0.07346	—	—	—
85.03	2.5	1.1127	—	—	—	—	0.3422	—	—	—	—	0.10087	—	—	—
122.4	3.0	0.9933	—	0.9936	—	—	0.3468	—	—	—	—	0.12276	—	—	—

[a] Static exchange approximation, HF orbitals, this work.
[b] Static exchange approximation, HF orbitals, Ref. [10].
[c] Static exchange approximation, Natural orbitals, Ref. [5].
[d] Static exchange approximation, Natural orbitals, Ref. [9].
[e] Polarization included, Ref. [5].

was chosen in such a way that the first increment was small enough to insure the accuracy of the trapezoid rule used for the first point in Eq. (28) and that Simpson's rule gave eight place accuracy on the integrals $\int_0^\infty R_{il}^2(x)x^2\,dx$. The structure of this grid is shown in Table II. By halving the increments and doubling the number of points per grid, the phase shift was changed only in the sixth decimal place. Therefore, it is felt that five place accuracy has been achieved. Extending the grid out to $20a_0$ gave no change in the eighth decimal.

For He the natural orbitals and occupation numbers of both Yarlagadda *et al.* [5] and Doll and Reinhardt [9] were used. Table III shows the comparison between the *s*, *p*, and *d* phase shifts using the HF density matrix, the renormalized density matrix and the accurate values which include polarization.

TABLE IV

Time and Storage Requirements for Calculating Phase Shifts

Type of phase shift	No. of outward integrations per phase shift	Ave. CPU time per phase shift (sec)	Core storage requirements (thousands of bytes)
He (Hartree–Fock) *s*, *p*, & *d*	2	2.5	100
Ne (Hartree–Fock) *s*,	3	5.2	100
p & *d*	4	7.6	100
He (natural orbitals, Ref. [9])			
s	10	20.3	100
p	15	39.5	120
d	17	43.8	120
He (natural orbitals, Ref. [5])			
s	15	41.3	120
p	24	88.4	140
d	28	93.6	140

All calculations were done on an IBM 370/155 computer. Table IV shows the time and storage requirements. All routines operate under a control program CON/360 written and kindly furnished by Nesbet [11]. CON/360 provides the I/O routines which make the point by point processing of the sequential data sets very efficient as well as a linking loader for dynamically overlaying unneeded routines and various other services for efficient use of the users main storage area.

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