Correlation effects in low-energy scattering of electrons by a model negative ion

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Abstract. This paper presents the results of first-order Bethe–Goldstone (BG) calculations of electron scattering from a two-electron model of a negative ion. The results of the BG calculations are compared to those obtained using several approximate polarisation potentials. The BG calculations appear to contain significant contributions from dynamical effects that are not incorporated in a formulation based on adiabatic (static) polarisation potentials, but that can be represented at least partially if the polarisability is treated as a frequency-dependent function.

1. Introduction

In order to assess the relative importance of different contributions to correlation effects in electron–atom scattering, we have performed a Bethe–Goldstone calculation of electron scattering from a two-electron model of a negative ion. Because we expect correlation effects, especially energy-dependent correlation effects, to be largest in a highly polarisable system, we have chosen the parameters of our model system to resemble $\text{H}^-$ as much as possible. The model should give a good portrayal of the behaviour of electron scattering by alkali negative ions as well.

Since the first low-energy calculations of electron–hydrogen scattering by MacDougall (1930) and by Morse and Allis (1931), considerable effort has been made to include correlation effects in low-energy scattering. These attempts may be roughly divided into two categories: calculations based on a semi-empirical analysis (Temkin and Lamkin 1961, La Bahn and Callaway 1966, Duxler et al 1971 and references therein), and calculations based on approximations of a formally derived theory (Burke and Schey 1962, Mittleman 1965, Nesbet 1967, Schneider et al 1970, Soukup 1973). The semi-empirical calculations assume that the polarisation is a single scalar constant, i.e. that the atomic electrons can adjust instantaneously to the changing position of the incident electron. Thus, these calculations do not include polarisation effects that depend on the velocity of the incident electron. The success of the calculations mentioned above, which are based on approximations to a formally exact theory, demonstrates the necessity for consistent inclusion of correlation effects other than the direct polarisation potential. Consequently, we have chosen to use Nesbet’s version of the Bethe–Goldstone (BG) method (Nesbet 1967) for our calculations.

As in bound-state problems, when correlation effects are included in scattering problems, the difficulty increases with each additional electron. Consequently, it is

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useful to apply to the problem of electron-atom scattering those bound-state methods, such as the model potential method (Bardsley 1974 and references therein), which reduce the number of electrons in the calculation. We hope that the model potential we use in these calculations will form a basis for calculating electron scattering from complex targets with two valence electrons.

The plan of this paper is as follows. The Bethe–Goldstone theory is reviewed briefly in § 2. In order to interpret the physical content of the approximations in the Bethe–Goldstone hierarchy, we have performed several calculations with physically derived approximations to the polarisation potential; these approximations are discussed in § 3. The model potential is presented in § 4 and details of the calculation are given in § 5. The results are discussed in § 6.

2. Review of the Bethe–Goldstone scattering theory

Many of the theories used as the basis for electron-atom scattering calculations are based on the reduction of the many-particle Schrödinger equation to a one-particle equation with an effective potential (Burke and Schey 1962, Mittleman 1965, Kleinman et al 1968, Schneider et al 1970). In contrast to the use of a one-electron effective Hamiltonian, the Bethe–Goldstone theory (Bethe and Goldstone 1957) reduces the Schrödinger equation to a series of two-electron equations. This concept was first applied to scattering problems by Temkin (1962), Mittleman (1966) and Nesbet (1967). The calculations in this paper are based on Nesbet's generalisation of the Bethe–Goldstone equations (Nesbet 1965), which is reviewed briefly in this section.

In Nesbet's generalisation a hierarchy of equations for \( n \) interacting electrons in the field of the remaining \( N - n \) electrons is constructed. The \( N \)th-order equation gives the exact wavefunction, so this hierarchy of Bethe–Goldstone (BG) equations should produce a convergent series for physical properties of the wavefunction.

For the \( (N + 1) \)-electron scattering problem (Nesbet 1967), the zeroth-order BG wavefunction is

\[
\Psi_0 = \Phi_0^k = (N + 1)^{-1/2} \det \phi_1(1) \ldots \phi_N(N)\phi_0^0(N + 1) = A \Phi_0 \phi_0^0
\]

(1)

where \( \phi_0^0 \) is the continuum solution of the Hartree–Fock equation with energy \( \frac{1}{2}k^2 \) and \( A \) is an antisymmetriser. The \( \phi_i \) form a complete set of bound (spin) orbitals ordered so that the first \( N \) are the occupied orbitals \( \phi_{i_1, \ldots, i_N} \), \( i_1 < \ldots < N \) and the rest are the unoccupied orbitals, \( \phi_{a_1, b_1, \ldots, a_b} \), \( a_1 < a_2 < \ldots < b \). A complete set of \( N \)-electron Slater determinants, \( \{ \Phi_\mu \} \), can be constructed from \( \Phi_0 \) by replacing occupied orbitals by unoccupied orbitals. In general \( \Phi_\mu \) can be expressed as

\[
\Phi_\mu = \Phi_{ijk}^{abc} \quad i < j < \ldots < N < a < b \ldots
\]

(2)

where the notation implies that orbitals \( ijk \) are replaced by \( abc \) in that order. Likewise, a complete set of \( (N + 1) \)-electron determinants can be constructed by adding unoccupied orbitals to \( \Phi_\mu \), giving \( \phi^a_\mu \).

The first-order BG calculation for scattering is a set of \( N \) calculations for the \( N \) \( \Psi_i \) where

\[
\Psi_i = \Phi^k + \sum_{ab} \Phi_{i}^{ab} \epsilon_{i}^{ab}
\]

(3)

\[
\Phi^k = \det \phi_1(1) \ldots \phi_N(N)\phi_k(N + 1)
\]

and \( \phi_k \) is a continuum orbital.
The effective potential implicitly contained in the first-order BG equations is energy-dependent and contains only those terms due to the excitation of orbital $i$. The two-particle Bethe–Goldstone equations for the incident electron and one atomic electron can be derived by separating the other $N-1$ electrons from a pair function $\chi_{ik}$, thus:

$$\Psi_i = A \Phi_i (1 \ldots N-1) \chi_{ik} (N, N+1)$$

in which the pair function can be written as superposition of pair configurations:

$$\chi_{ik} = \det \left( \phi_i (N) \phi_k (N+1) + \sum_{ab} \phi_a (N) \phi_b (N+1) c_{ab} \right)$$

(4)

and $A$ antisymmetrises $\Psi_i$. The BG equation for $\chi_{ik}$ follows from the conditions that

$$\langle \Phi_i | H - E | \Psi_i \rangle = 0$$

(6)

(or equivalently, from the condition that the functional derivative of $\langle \Psi_i | H - E | \Psi_i \rangle$, taken with respect to variations of $\chi_{ik}$, must vanish), and that $\chi_{ik}$ is orthogonal to the $N-1$ orbitals of $\Phi_i$. These conditions result in the equation for $\chi_{ik}$, which was first derived by Mittleman (1966) for electron–alkali-atom scattering:

$$[-\frac{1}{2} \nabla_0^2 - \frac{1}{2} \nabla_i^2 + V_{HF}(0) + V_{HF}(1) + (1 - K_p)/r_{10} - \frac{1}{2} k^2 - E_a + E_{a'}] \chi_{ik} = 0.$$ 

(7)

In this equation

$$V_{HF} = -Z/r_0 + \sum_{i=1}^{N-1} \langle \phi_i (1) | R (0, 1) | \phi_i (1) \rangle$$

$$R (0, 2) = (1 - P_{01})/r_{02}$$

$$E_{a'} = \langle \Phi_i | H | \Phi_i \rangle$$

$P_{01}$ is a permutation operator and $K_p$ is the projection operator that orthogonalises $\chi_{ik}$ to the $N-1$ orbitals of $\Phi_i$. The expansion for $\chi_{ik}$ (equation (5)) further reduces equation (7) to a one-electron equation for $\Phi_i$. Since each $\phi_i$ satisfies a different equation (depending on $i$) and is also different from $\phi_{i'}$, the zeroth-order phaseshifting $\delta_i(0)$, which are the total phaseshifting for the zeroth-order function $\phi_i$, are different from the phaseshifting $\Delta_i(i)$ of the first-order functions $\phi_i$. The first-order net phaseshifting, $\delta_i(i)$, which are the differences between the phaseshifting of the first-order functions and the zeroth-order functions, are defined as

$$\delta_i(i) = \Delta_i(i) - \delta_i(0).$$

(9)

The total first-order phaseshifting, $\delta_i$, are given by

$$\delta_i = \delta_i(0) + \sum_{i} \delta_i(i).$$

(10)

Higher order BG equations and the corresponding higher order phaseshifting can also be defined (Nesbet 1967); however, we expect the higher order phaseshifting to be small so that the first-order phaseshifting should be a good approximation.

The BG hierarchy for scattering of electron 0 from a two-electron target, containing electrons 1 and 2 has the following structure: if the reference state $\Phi_0$ is a single Slater determinant, the zeroth-order BG equation is equivalent to a static exchange approximation, in which all polarisation and correlation effects are neglected. The first-order
BG problem should be considered as a set of three equations. The two BG equations for the pairs (0, 1) and (0, 2) introduce correlation primarily between the incident electron and one target electron. Correlation between the target pair (1, 2), which should also be included at this order of approximation, results in a third equation which is equivalent to a static exchange calculation for scattering from a target described by a correlated wavefunction. The second-order BG equation is for the set (0, 1, 2), and would give the exact solution of the three-electron problem, but we will not attempt to solve this equation.

Although the BG formalism, as well as other methods for including correlation effects in scattering calculations, is capable of including intra-target correlation, these effects have been omitted from this calculation. Calculations by Le Dourneuf et al (1976), Thomas et al (1974) and Harris and Michels (1971) indicate that, while intra-target correlation is important in determining the positions of low-energy resonances, it is not nearly as important as projectile–target correlation (primarily polarisation) for energies away from resonances.

3. Approximations to the effective potential

In order to interpret the physical content of the approximations in the BG hierarchy, we have performed several calculations with physically plausible approximations to the one-electron effective potential, $V_{\text{eff}}$ (Kleinman et al 1968). The one-particle function, $\phi_k$, which gives the exact scattering amplitude satisfies the equation

$$(K - V_{\text{eff}} - E_k)\phi_k = 0$$

(11)

where $K$ is the kinetic energy operator and $E_k = \frac{1}{2}k^2$ is the energy of the incident electron. It is convenient to write $V_{\text{eff}}$ as

$$V_{\text{eff}} = V_{\text{HF}} + V_{\text{pol}}$$

(12)

where $V_{\text{HF}}$ is the Hartree–Fock potential and $V_{\text{pol}}$ describes the polarisation of the target by the incident electron. The approximations to $V_{\text{pol}}$ which we have used are discussed in this section and the resulting phaseshifts are compared to the first-order BG phaseshifts in § 6.

Before discussing approximations to $V_{\text{pol}}$, it is useful to discuss the physical effects this term represents. At large distances the major effect of the interaction between the incident electron and the target is polarisation of the target. Because the incident electron is moving, the polarisation potential should depend on the velocity of the electron as well as on its position. The attractive polarisation potential increases the velocity of the incoming electron (relative to its value in the absence of a polarisation potential) and the change in velocity in turn affects the polarisation potential. Consequently, the electron–atom scattering process is fundamentally a dynamical many-body problem.

The simplest approximation beyond which the Hartree–Fock still retains part of $V_{\text{pol}}$ is the adiabatic approximation, which assumes that the atomic electrons can adjust instantaneously to the change in position of the incident electron. Formal expressions for the adiabatic approximation to $V_{\text{pol}}$ have been derived by Mittleman (1965) and Kleinman et al (1968). We can write their results as

$$V_{\text{pol}} \sim V_{\text{ad}}^{(1)} + V_{\text{ad}}^{(2)}$$

(13)
where the asymptotic form of \( V_{ad}^{(1)} \) is given by

\[
V_{ad}^{(1)} \to -\frac{1}{2} \sum_{i=1}^{\infty} \frac{\alpha_i}{r^{(2i-2)}}
\]  

(14)

and

\[
V_{ad}^{(2)} \to 3\beta_1/r^6.
\]

In these equations \( \alpha_i \) is a static multipole polarisability and \( \beta_1 \) is equivalent to the spectroscopic statistical moment \( \mu_1(-2) \) or \( S(-3) \) (Kleinman et al 1968). \( V_{ad}^{(2)} \) is usually called the ‘non-adiabatic’ correction even though it is based on the assumption that the energy of the incoming electron is small. It has been found (LaBahn and Callaway 1966) that use of \( V_{ad}^{(1)} \) without \( V_{ad}^{(2)} \) results in a potential which is too attractive because \( 6\beta_1 \) is often the same order of magnitude as \( \alpha_2 \).

The first approximation that we have used is the first-order adiabatic approximation in which we take

\[
V_{pol} \sim V_{ad}^{(1)} \sim V_{ad}^{i=1} + V_{ad}^{i=2}
\]

(15)

where the dipole and quadrupole contributions are given by the Bethe–Reeh expressions (Reeh 1960) in terms of scaled variables:

\[
V_{ad}^{i=1}(u) = -\frac{9}{2u^2}[1 - \frac{1}{3} e^{-2u}(1 + 2u + 6u^2 + 20u^3 + 15u^4)] - \frac{1}{3} e^{-4u}(1 + u^4)
\]

(16)

and

\[
V_{ad}^{i=2}(y) = -\frac{15}{2y^6}[1 - 2e^{-2y}(1 + 2y + 3y^2 + 5y^3 + 7y^4 + 9y^5 + 11y^6 - 135y^8 - 135y^9)] + e^{-4y}(1 + 4y + \frac{20}{3}y^2 + 6y^3 + \frac{28}{9}y^4 + \frac{8}{9}y^5 + \frac{8}{9}y^6) + \frac{8}{135}y^{10} Ei(-2y)].
\]

(17)

In these equations \( Ei(x) \) is the exponential integral (Abramowitz and Stegun 1968; equation (5.1.2)) and \( u \) and \( y \) are defined by

\[
u = z_1 r \quad y = z_2 r
\]

(18)

where

\[
z_1^4 = 9/\alpha_1 \quad z_2^6 = 15/\alpha_2
\]

and \( \alpha_1 \) and \( \alpha_2 \) are the dipole and quadrupole polarisabilities. The asymptotic form of \( V_{pol}^{ad} \) is

\[
V_{pol}^{ad} \sim -\frac{1}{2}(\alpha_1/r^4 + \alpha_2/r^6).
\]

(19)

This polarisation potential was used by McDowell (1968) to calculate electron–H− scattering, and is also the form of the \( l = 1 \) and \( 2 \) components of the adiabatic potential used in the polarised-orbital calculations of LaBahn and Callaway (1964, 1966) and Callaway et al (1968).

The second approximation that we have used is the second-order adiabatic approximation in which we take

\[
V_{pol} \sim V_{pol}^{so} = V_{ad}^{i=1} + V_{ad}^{i=2}
\]

(20)

where \( V_{ad}^{i=1} \) is defined by equation (16) and \( V_{ad}^{i=2} \) is obtained by replacing \( 15/2y^6 \) in equation (17) by \( (\alpha_2 - 6\beta_1)/2r^6 \). The asymptotic form of \( V_{pol}^{so} \) is then

\[
V_{pol}^{so} \sim -\frac{1}{2}(\alpha_1/r^4 + (\alpha_2 - 6\beta_1)/r^6).
\]

(21)
The third approximation that we have used is a non-adiabatic approximation to $V_{\text{pol}}$ which is based on semi-empirical arguments. Several workers have suggested such potentials (Mittleman 1965, Jhanwar and Khare 1975, Onda 1971, Garrett 1969); the one we have used has the asymptotic form of the classical cut-off (Buckingham) polarisation potential used by Mittleman (1965) and Jhanwar and Khare (1975). The explicit form that we used is given by

$$V_{\text{pol}}^{\text{Buck}} = V_{l=1}^{\text{Buck}} + V_{l=2}^{\text{sd}}$$

where $V_{l=2}$ is given by equation (17) and $V_{l=1}^{\text{Buck}}$ is obtained by replacing $9/(2u^4)$ in equation (16) by $\frac{3}{2} \alpha_1/[\pi^2 + (k/\Delta)^2]^2$ where $\Delta$ is an average atomic excitation energy. The asymptotic form of $V_{\text{pol}}^{\text{Buck}}$, a form with no particular physical basis, is then

$$V_{\text{pol}}^{\text{Buck}} \sim -\frac{3}{2}(\alpha_1/[\pi^2 + (k/\Delta)^2]^2 + \alpha_2/r^6)$$

As the results presented in § 6 will show, none of these three approximations to $V_{\text{pol}}$ adequately predicts polarisation effects in electron–H$^-$ scattering. The failure of these approximations can be understood by considering the conditions for the validity of the adiabatic approximation. As shown by Mittleman and Watson (1959), the condition for both the first- and second-order adiabatic approximations is that the ratio of the average virtual excitation energies of the incident electron to those of the atomic electrons must be less than one. This condition for the adiabatic assumption can be expressed in another way: the energy range of virtual excitations of the incident electron must be small compared to the energy range for changes in $\alpha(w)$, where $\alpha(w)$ is a frequency-dependent polarisability (see equations (69) and (70) of Csanak and Taylor (1972)). When the probability of large fluctuations in the energy of the incident electron is small, the adiabatic assumption is valid and one can use the static polarisability constants as in equation (14).

For the case of electron–H$^-$ scattering, one of the critical factors resulting in the breakdown of the adiabatic assumption is the small detachment energy. If the average atomic excitation, $\Delta$, is assumed to be the order of magnitude of the ionisation potential (Dalgarno 1962), then $\Delta$ for H$^-$ is much smaller than $\Delta$ for H. Since the rate of convergence of the adiabatic expansion depends on the size of $\Delta$, the adiabatic expansion for H$^-$ is less likely to converge than that for H if the magnitudes of the average virtual excitations are the same. Another result of the small detachment energy of H$^-$ is that the energy range over which $\alpha_1(w)$ is constant is very small, as shown by figure 1. Figure 1 is a plot of $\alpha_1(w)$ for H$^-$ as calculated by Adelman’s approximation (Adelman 1972, equation (31)), for $\alpha_1(0) = 212$ au (Schwartz 1961). The requirement that the energy range of virtual excitations of the incident electron must be small compared to the range for changes in $\alpha_1(w)$, represents a severe restriction in the case of electron–H$^-$ scattering.

A simple method for approximating the non-adiabatic effects in $V_{\text{pol}}$ can be devised by considering the physical process involved. This term in the potential describes the response of the target electrons to the time-dependent field produced by the incident electron. If the field at the nucleus due to the incident electron, $E(t)$, were known, then an average polarisability, $\langle \alpha(w) \rangle$, could be defined as

$$\langle \alpha(w) \rangle = \left( \int_0^\infty \alpha(w) f(w) \, dw \right) \left( \int_0^\infty f(w) \, dw \right)^{-1}$$

(24)
where \( f(\omega) \) is the Fourier transform of the field:

\[
f(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(-i\omega t)E(t). \tag{25}
\]

However, since \( E(t) \) depends on the velocity of the incident electron, which in turn depends on the polarisation potential, \( E(t) \) must be approximated. The first approximation that comes to mind is to replace \( E(t) \) by the field due to an electron with incident energy \( \frac{1}{2}k^2 \) moving in the potential \( \frac{1}{r} \). However, it is well known that for Coulomb scattering \( r(t) \) can only be obtained by solving a transcendental equation, which would make evaluation of equation (24) intractable.

An approximation at the other extreme can be obtained by assuming that \( k \) is constant. This case is illustrated by figure 2. In this figure \( a \) is the distance of closest approach and \( t = 0 \) corresponds to \( r_{01} = a \). The field at the nucleus (point 0) is

\[
E(t) = \frac{1}{(a^2 + k^2t^2)} \tag{26}
\]

because \( r(t) = kt \). For this \( E(t) \), \( f(\omega) \) is given by

\[
f(\omega) = (2ak)^{-1} \exp(-|a\omega/k|). \tag{27}
\]

The distance of closest approach can be related to the angular momentum by using the semiclassical relation, \( a = (l + \frac{1}{2})/k \) (Massey and Burhop 1969, p 392).

The average dipole polarisability, \( \langle \alpha_1(\omega) \rangle \), calculated from equations (24) and (27) is substituted for \( \alpha_1 \) in equation (16) to give an approximate polarisation potential with

![Figure 2. Scattering geometry.](image)
the asymptotic form:

\[ V_{\text{pol}}^w \sim -\frac{1}{2} (\langle \alpha_1(\omega) \rangle/r^4 + \alpha_2/r^6). \]  

(28)

For higher energies at which \( \langle \alpha_1(\omega) \rangle \) is much less than \( \alpha_1(0) \), the quadrupole polarisability should also be replaced by its average value.

Although the approximations used to derive this expression for \( E(t) \) are questionable for small \( l \) and for low energies, they should be better for higher \( l \) and at higher energies. These calculations are done, therefore, to obtain a qualitative estimate of the type and magnitude of frequency-dependent polarisation effects.

Since these calculations were performed, Seaton and Steenan-Clark (1977) have shown that the effective potential for electron–atom scattering has the asymptotic form

\[ V_{\text{pol}} \sim -\alpha_1 r^{-4} - (\alpha_2 - 6\beta_1 - 24\gamma k^2) r^{-6} - \delta r^{-7} + O(r^{-8}) \]  

(29)

at energies below the inelastic threshold. Both this potential and \( V_{\text{pol}}^{\text{Buck}} \) contain \( k^2/r^6 \) terms but with different constants. In both cases the non-adiabatic term would tend to decrease the phaseshifts.

Phaseshifts for these approximations to the effective potential can be calculated by solving equation (11) with the approximate polarisation potential in place of \( V_{\text{pol}} \) (equation (12)). (These calculations are static exchange calculations with a local polarisation potential.) The resulting phaseshifts \( \Delta^a \) (\( a \) denotes an approximation) can be expressed as the sum of \( \delta_i(0) \) and a term describing the change due to \( V_{\text{pol}}^a, \delta_i(a) \):

\[ \Delta^a = \delta_i(0) + \delta_i(a). \]  

(30)

For the model potential calculations, \( \delta_i(a) \) can be compared to \( \delta_i \) (obtained from the BG calculations) to evaluate the approximation \( V_{\text{pol}}^a \). Insofar as correlation effects are insensitive to the nuclear potential, \( \delta_i(a) \) and also \( \delta_i^1 \) should be transferable to electron–H\(^+\) scattering.

4. Model potential

In recent years model potentials and pseudopotentials have been widely used to calculate properties of bound systems (Bardsley 1974). The basic motivation for using these potentials is the belief that many properties of atoms and molecules are determined primarily by the interactions among the valence electrons. In the pseudopotential approach, the core electrons are replaced by a strongly repulsive potential which keeps the 'pseudo-electrons' out of the core. Consequently, the pseudofunction is insensitive to the exact form of the potential. The pseudopotential approach has been successfully applied to the study of alkali negative ions (Hotop and Lineberger 1975) and to the calculation of wavefunctions for electron–atom scattering, photodetachment and photoionisation (Tully 1969, Schneider et al 1969).

A slightly different approach has been used by Kestner and Sinanoglu (1962) to study electron correlation in helium-like systems using a model potential. In their model, the nuclear potential is replaced by a harmonic oscillator potential while the Coulomb repulsion between the two electrons is retained. Their motivation in choosing this model was that the correlation part of the wavefunction and the correlation energy should be fairly insensitive to the central field (Kestner and Sinanoglu 1962, Lowdin 1959).
We have performed a model potential calculation of electron scattering from H\(^-\) with two objectives in mind. The first is to try to find a model potential that can form a basis for a pseudopotential calculation of both elastic and inelastic electron scattering from complex targets with two valence electrons. The second is the hope that the changes in the phaseshifts due to correlation can be transferred to non-model systems, because we expect these changes to be less sensitive to the nuclear or core potential than the total phaseshifts.

To apply Kestner and Sinanoglu's model to a scattering problem, the nuclear potential must be modified to permit continuum solutions. The Hamiltonian for the ionic model used in our scattering calculations is

\[
H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + V_n(r_1) + V_n(r_2) + r_1^{-1}r_2^{-1}
\]

where the model potential \(V_n(r)\) is

\[
V_n(r) = \begin{cases} 
\frac{1}{2}fr^2 - V_0 & r \leq R_0 \\
-r^{-1} & r \geq R_0.
\end{cases}
\]

The properties of the model ion depend on the choice of \(f\), \(R_0\) and \(V_0\), with the restriction that the potential be continuous. In order for the model to describe accurately scattering from a real atom with two valence electrons, it is important that the detachment energy of the model system match that of the real system. Both the static and frequency-dependent polarisabilities for H\(^-\) have been shown (Adelman 1972) to be determined to a good approximation by the detachment energy. Since the dipole polarisation potential is the most important correlation correction in electron–atom scattering, correlation effects should also depend directly on the detachment energy of the model. Several choices of \(f\), \(R_0\), \(V_0\) were used to calculate approximate values of the detachment energy and polarisability of the model system (Valley 1977). The set which most closely modelled H\(^-\) was used in the phaseshift calculations. The model parameters and some model properties are given in table 1.

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<tr>
<th>Table 1. Model parameters and properties (distances in bohr, energies in hartree).</th>
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<td>Model potential parameters</td>
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<td>Minimum energy two-term function (d_1e^{-d_1r^2/2} + d_2e^{-d_2r^2/2})</td>
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<td>Detachment energy for model</td>
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<td>Dipole polarisability (\alpha_1)</td>
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\(^a\) Exact energy for model H energy, for model H\(^-\) calculated with two-term function.

\(^b\) Calculated by assuming the correlation energy for the model H\(^-\) is the same as Kestner and Sinanoglu's model.

\(^c\) Energies for model H and H\(^-\) both calculated with a two-term function.

\(^d\) Calculated by the method of Cohen and Roothaan (1965) and Cohen (1965).

\(^e\) Calculated using Adelman's formulae (Adelman 1972, equations (18) and (39)) and \(IP = 0.109\) au.
5. Details of the calculations

The zeroth- and first-order BG equations for scattering from the model potential are solved using a matrix variational method developed by Payne (1969, 1970). The wavefunctions in the one- and two-electron BG equations are expanded in partial waves and the equation for each partial wave is solved separately. We also integrate over spin and obtain two distinct first-order BG pair functions. In one case the two electrons have the same spin and the spatial wavefunction is denoted as $\chi_{ik}$ (or triplet pair). In the other case the electrons have opposite spin and the wavefunction is $\chi_{ik}$ (singlet pair). The one-electron spatial functions $\varphi_{L,k}$ and the two-electron functions $\chi_{L,ik}$ are expanded in basis sets:

$$\varphi_{L,k}(0) = \sum_{i=0}^L \psi_i(r_0) Y_L(\Omega_0) c_i$$

$$\psi_0(0) = (kr_0)^{-1} [F_L(kr_0) + \tan \eta_f (1-e^{-i|\Omega_0|})^{-1} G_L(kr_0)]$$

$$\psi_{i+1}(0) = r_0^i \exp(-\zeta r_0^2).$$

In these equations $F_L(x)$ and $G_L(x)$ are the regular and irregular Coulomb functions of angular momentum $L$ (Abramowitz and Stegun 1968, chap 14), $[a]_k$ indicates the greatest integer less than $a$, $\eta_f$ is the trial phaseshift and $\{n_i\}$ is the set of integers $\{L, L+2, L+4, \ldots\}$. The two-electron functions $\chi_{L,ik}$ are expanded as

$$\chi_{L,ik}(1,0) = \varphi(1) \sum_{i=0}^L \psi_i(0) Y_L(0) c_i + \sum_n \chi_{p_{n}q_{n},s} (1,0) \mathcal{Y}_{L,1,n,0} (\hat{r}_1, \hat{r}_0) c_n$$

where

$$\chi_{p_{n}q_{n},s} (1,0) = r_1^{p_n} r_0^{q_n} \exp[-\zeta (r_1^2 + r_0^2)]$$

$$\mathcal{Y}_{L,1,n,0} (\hat{r}_1, \hat{r}_0) = \sum_{m_L,m_s} C_{l_1,l_0}(L M_L; m_1,m_2) Y_{l_1}^{m_L}(\hat{r}_1) Y_{l_0}^{m_S}(\hat{r}_0).$$

The sum over $n$ includes $p_n \geq l_1; q_n \geq l_0; s_n \geq 0$ and $l_0 + l_1 + n \leq L + 1$. For $\chi_{p_{n}q_{n},s}$ functions with $s = 0, p$ and $q$ belong to the set $\{L, L+2, L+4, \ldots\}$. The specific basis set used for each calculation is denoted by $(n_1, n_2, n_3)$ where $n_1$ is the maximum value of $n_2$ equation (33), $n_2$ is the maximum value of $p + q$ for functions with $s = 0$ and $n_3$ is the maximum value of $p + q + s$ for functions with $s \neq 0$. The parameter $\zeta$ is a variational parameter which can be changed to accelerate the convergence of the basis set expansion. The value of $\zeta$ is the same for all basis functions in order to facilitate the evaluation of integrals.

The atomic function $\varphi$ used in these calculations is the two-term Gaussian function given in table 1.

6. Results and discussion

The zeroth- and first-order Bethe–Goldstone phaseshifts (mod $\pi$) for the model potential are given in tables 2, 3, 4 and in figures 3, 4 and 5. For $L = 0$, the phaseshift is actually $\pi$ plus the value given at $k = 0$. The first-order phaseshifts have been calculated only for S-wave, $L = 0$, and P-wave, $L = 1$, scattering since higher values of $L$ require evaluation of increasingly complex (and time-consuming) integrals. Correlation effects which cannot be described by a local polarisation potential should
become more insignificant as $L$ increases since the incident electron is kept out of the atomic region by the repulsive angular momentum term in the potential; therefore, calculations with an approximate polarisation potential should be adequate for higher $L$. For a Coulomb potential the phaseshifts are a very slowly decreasing function of $L$, so it is not feasible to calculate converged values of the differential cross section.

The zeroth- and first-order phaseshifts are defined by equations (9) and (10). Specifically, the phaseshift of the zeroth-order BG function $\varphi_{\ell,k}^0$ is $\delta_L(0)$; the phaseshifts of the first-order BG functions $\chi_{-}^\ell$ and $\chi_{+}^\ell$ are $\Delta_L(-)$ and $\Delta_L(+)$ respectively. The first-order net increments are $\delta_L(-) = \Delta_L(-) - \delta_L(0)$ and $\delta_L(+) = \Delta_L(+) - \delta_L(0)$, and the first-order phaseshift $\delta_L^{(1)}$ is given by $\delta_L^{(1)} = \delta_L(0) + \delta_L(+) + \delta_L(-)$. The zeroth-order phaseshift calculations are well behaved in terms of their convergence as additional basis functions are added and in terms of their behaviour as a function of $\zeta$ (see equations (33) and (34)). The zeroth-order phases are usually calculated with the basis set $(22, 0, 0)$ which has 13 basis functions for $L = 0$ and 12 for $L = 1$. For a given $\zeta$, use of more than 7 of these basis functions does not change the phaseshift by more than 0.1% and, for a given number of functions, changing $\zeta$ by 30% changes the phaseshift by less than 0.1%. In contrast to the zeroth-order phases, the phaseshifts of the first-order BG functions $\chi_{-}^\ell$ and $\chi_{+}^\ell$, $\Delta_0(-)$ and $\Delta_0(+)$, are not as well behaved. For $L = 0$, the first-order wavefunctions are calculated with the basis $(6, 2, 3)$ for $\chi_{-}^0$ and with basis sets up to $(6, 6, 6)$ for $\chi_{+}^0$. For $\chi_{-}^0$ the basis set $(6, 6, 6)$ has 31 functions (five $\psi_1$ functions, four $\chi_{pq0}$ functions and 22 $\chi_{pq\ell}$ functions) while the sets $(6, 4, 4)$ and $(6, 4, 5)$ have 14 and 20 functions respectively. The phaseshift of $\chi_{-}^0$, $\Delta_0(-)$, is given in table 2 and in figure 3 for four basis sets. The results for 14 functions are for the basis $(6, 4, 4)$, while the other results are for the first 20, 24 or 29 functions of the basis set $(6, 6, 6)$. The values for 29 functions are identical to those given for $\Delta_0(-)$, $(6, 6, 6)$ in table 3 and figure 4. As additional basis functions are added, the convergence is slow and irregular, particularly for energies greater than 0.04 au. Lack of

<table>
<thead>
<tr>
<th>$E_k = \frac{1}{2}k^2$ (Hartree)</th>
<th>Number of functions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14</td>
</tr>
<tr>
<td>0.01125</td>
<td>0.591 x 10^-5</td>
</tr>
<tr>
<td>0.02</td>
<td>0.000476</td>
</tr>
<tr>
<td>0.0242</td>
<td>0.001153</td>
</tr>
<tr>
<td>0.02645</td>
<td>0.003071</td>
</tr>
<tr>
<td>0.03125</td>
<td>0.004011</td>
</tr>
<tr>
<td>0.03645</td>
<td>0.004150</td>
</tr>
<tr>
<td>0.0392</td>
<td>0.004539</td>
</tr>
<tr>
<td>0.045</td>
<td>0.004871</td>
</tr>
<tr>
<td>0.04805</td>
<td>0.004937</td>
</tr>
<tr>
<td>0.0512</td>
<td>0.004978</td>
</tr>
<tr>
<td>0.05445</td>
<td>0.005695</td>
</tr>
<tr>
<td>0.05615</td>
<td>0.006354</td>
</tr>
<tr>
<td>0.08</td>
<td>0.00674</td>
</tr>
<tr>
<td>0.082</td>
<td>0.006252</td>
</tr>
<tr>
<td>0.09245</td>
<td>0.00598</td>
</tr>
<tr>
<td>0.10125</td>
<td>0.005393</td>
</tr>
</tbody>
</table>
Table 3. $S$ phaseshifts for model potential: phase $-\pi$.

<table>
<thead>
<tr>
<th>$E_k = \frac{1}{2} k^2$ (Hartree)</th>
<th>$\delta_0(0)$ (22, 0, 0)</th>
<th>$\Delta_0(-)$ (6, 6, 6)</th>
<th>$\Delta_0(\pi)$ (6, 2, 3)</th>
<th>$\delta_0^{(1)}$ first-order phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01125</td>
<td>-0.107 x $10^{-10}$</td>
<td>0.591 x $10^{-5}$</td>
<td>-0.7 x $10^{-6}$</td>
<td>0.66 x $10^{-5}$</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.59 x $10^{-9}$</td>
<td>0.000609</td>
<td>0.5815 x $10^{-4}$</td>
<td>0.000667</td>
</tr>
<tr>
<td>0.0242</td>
<td>0.001404</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02645</td>
<td>0.002549</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03125</td>
<td>-0.269 x $10^{-6}$</td>
<td>0.003893</td>
<td>0.0008802</td>
<td>0.004773</td>
</tr>
<tr>
<td>0.03645</td>
<td>0.004695</td>
<td></td>
<td></td>
<td>0.00575</td>
</tr>
<tr>
<td>0.0392</td>
<td>0.004966</td>
<td></td>
<td></td>
<td>0.00611</td>
</tr>
<tr>
<td>0.045</td>
<td>-0.1471 x $10^{-4}$</td>
<td>0.008060</td>
<td>0.001049</td>
<td>0.009124</td>
</tr>
<tr>
<td>0.04805</td>
<td>0.008783</td>
<td></td>
<td></td>
<td>0.01007</td>
</tr>
<tr>
<td>0.0512</td>
<td>0.008866</td>
<td></td>
<td></td>
<td>0.00931</td>
</tr>
<tr>
<td>0.05445</td>
<td>0.008511</td>
<td></td>
<td></td>
<td>0.00888</td>
</tr>
<tr>
<td>0.06125</td>
<td>0.008297</td>
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<td></td>
<td>0.007258</td>
</tr>
<tr>
<td>0.06845</td>
<td>-0.0005623</td>
<td>0.008845</td>
<td>0.0005567</td>
<td>0.00964</td>
</tr>
<tr>
<td>0.08</td>
<td>-0.001720</td>
<td>0.009875</td>
<td>-0.0001901</td>
<td>0.01140</td>
</tr>
<tr>
<td>0.0882</td>
<td>-0.003258</td>
<td>0.01018</td>
<td>-0.001325</td>
<td>0.01212</td>
</tr>
<tr>
<td>0.09245</td>
<td>-0.004360</td>
<td></td>
<td>-0.002187</td>
<td></td>
</tr>
<tr>
<td>0.10125</td>
<td>-0.007432</td>
<td>0.008538</td>
<td>-0.004712</td>
<td>0.01126</td>
</tr>
</tbody>
</table>

Figure 3. BG $\Delta_0(-)$ phaseshifts for model potential as a function of basis set size: $\bigcirc$, 14 functions; $\Delta$, 20 functions; $+$, 24 functions; $\times$, 29 functions.

Figure 4. BG $S$ phaseshifts for model potential: $+$, $\delta_0(0)$ (22, 0, 0); $\bigcirc$, $\Delta_0(-)$ (6, 6, 6); $\triangle$, $\Delta_0(\pi)$ (6, 2, 3); $\times$, $\delta_0^{(1)}$ first-order phase.
convergence for energies greater than the detachment energy probably reflects the fact that there is significant coupling with the detachment channel, and that this coupling is not explicitly included in the basis set. The detachment channel is partially represented by the \( \chi_{pq} \) functions, particularly by those with large values of \( \langle r_1^2 + r_2^2 \rangle \) and \( \langle r_1^2 \rangle \). Consequently, addition of \( \chi_{pq} \) functions with larger values of \( n_3(=p+q+s) \) causes a large change in the phaseshift. The addition of \( \chi_{pq0} \) functions to the \( \phi \psi_i \) functions causes a large change in the phaseshift, but if the \( \chi_{pq0} \) functions are added after \( \chi_{pq} \) functions with the same sum of powers, they change the phaseshift very little. Addition of basis functions to the calculation for \( E_k < 0.03125 \) au should not change the phaseshift by more than 10%. On the other hand, addition of functions for \( E_k > 0.06125 \) au may change the phaseshift by 20% or 30%. The first-order phaseshifts are also much more sensitive to changes in \( \zeta \).

The phaseshift of \( x_0, \Delta_0(+) \) (for \( L = 0 \)) is also given in table 3 and figure 4. Considering that fewer basis functions are used (there are 14 functions for the basis (6, 2, 3)), the phaseshifts seem better converged in terms of the basis set. Addition of basis functions could change the phaseshift by 20%. However, because \( \delta_0(+) \) is smaller than \( \delta_0(-) \) and since the matrix elements are much more time consuming to evaluate, it is not considered worthwhile to increase the number of basis functions. The convergence does not deteriorate as much as the energy increases, but the same sensitivity to \( \zeta \) occurs.

The first-order phaseshifts for \( L = 1, \Delta_1(-), \Delta_1(+) \) and \( \delta_1^{(1)} \) are given in table 4 and figure 5. The wavefunctions \( x_\pm \) and \( \chi_1^+ \) are calculated with the basis sets (5, 0, 4) and (5, 0, 3), respectively. Functions of the type \( \chi_{pq0} \) are omitted from these calculations because the \( L = 0 \) calculations demonstrate that they do not contribute significantly to the phaseshift. Unlike the \( L = 0 \) phase \( \Delta_0(-) \), the convergence in the number of basis functions of the \( L = 1 \) phase \( \Delta_1(-) \) seems to be somewhat better at higher energies. The phaseshifts probably would not change by more than 20% if more basis functions were added; however, the phaseshifts are again fairly sensitive to the choice of \( \zeta \). The phaseshift for \( x_1^+, \Delta_1(+) \) is again much smaller than \( \Delta_1(-) \) and its calculation is the most time consuming, so relatively little effort was spent optimising \( \zeta \). The addition of basis functions here would require unjustifiably large amounts of computer time.

### Table 4. P phaseshifts for model potential.

<table>
<thead>
<tr>
<th>( E_k = \frac{1}{2} k^2 ) (Hartree)</th>
<th>( \delta_1(0) ) (21, 0, 0)</th>
<th>( \Delta_1(-) ) (5, 0, 4)</th>
<th>( \Delta_1(+) ) (5, 0, 3)</th>
<th>( \delta_1^{(1)} ) first-order phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01125</td>
<td>0.414 \times 10^{-10}</td>
<td>0.393 \times 10^{-10}</td>
<td>0.30 \times 10^{-10}</td>
<td>0.414 \times 10^{-10}</td>
</tr>
<tr>
<td>0.02</td>
<td>0.206 \times 10^{-5}</td>
<td>0.0041</td>
<td>0.0009733</td>
<td>0.817 \times 10^{-4}</td>
</tr>
<tr>
<td>0.03</td>
<td>0.126 \times 10^{-5}</td>
<td>0.01298</td>
<td>0.000377</td>
<td>0.00168</td>
</tr>
<tr>
<td>0.045</td>
<td>0.01656</td>
<td>0.01949</td>
<td>0.002195</td>
<td>0.00377</td>
</tr>
<tr>
<td>0.048</td>
<td>0.01949</td>
<td>0.02195</td>
<td>0.00377</td>
<td>0.00377</td>
</tr>
<tr>
<td>0.049</td>
<td>0.0231 \times 10^{-4}</td>
<td>0.00542</td>
<td>0.00377</td>
<td>0.00377</td>
</tr>
<tr>
<td>0.051</td>
<td>0.0001978</td>
<td>0.00542</td>
<td>0.00377</td>
<td>0.00377</td>
</tr>
<tr>
<td>0.052</td>
<td>0.009933</td>
<td>0.00542</td>
<td>0.00377</td>
<td>0.00377</td>
</tr>
<tr>
<td>0.054</td>
<td>0.003542</td>
<td>0.00752</td>
<td>0.00377</td>
<td>0.00377</td>
</tr>
</tbody>
</table>
Figure 5. BG P phaseshifts for model potential: +, $\delta_1(0) (21, 0, 0); \bigcirc, \Delta_1(-) (5, 0, 4); \bigtriangleup, \Delta_1(+) (5, 0, 3); \times, \delta_1^1$ first-order phase.

Perhaps the most interesting feature of the first-order phaseshifts is the structure in the curve for $\Delta_0(-)$ at approximately $E_k = 0.05$ au (figures 3 and 4). Although this bulge, suggestive of a discontinuity, in the slope of $\Delta_0(-)$ as a function of $E_k$ is not as noticeable in the phaseshift curves for 14 or 20 functions, this feature seems to be real and not just an artifact due to the lack of convergence of the basis set. There is also a corresponding flattening of the $\Delta_0(+)$ curve in the same energy region and $\Delta_1(-)$ changes slope at about the same point. If real, these features probably occur at or very close to the detachment threshold. Similar discontinuities in the slope of the S, P and D phaseshifts at the 2p threshold in electron–Li scattering have been found by Burke and Taylor (1969) and Bardsley and Nesbet (1973). They find that, although these discontinuities may correspond to a cusp in the partial cross section for elastic scattering at the threshold, the discontinuities in the slope of the phaseshifts can also be consistent with a smooth variation of the elastic scattering partial cross section (Bardsley and Nesbet 1973). The analysis of Fonda and Newton (1959) indicates that, in the case of a detachment channel in which there is a Coulomb repulsion between particles in the new channel, there should be no cusp in the differential cross section.

The variation in the slope of $\Delta_0(-)$ could be due to an unresolved resonance just below the threshold. Further calculations for $E_k = 0.045$ au indicate that the increase in the phaseshift is due primarily to the addition of basis functions which allow one electron to be much further from the atom than the other. In other words, basis functions which primarily increase radial correlation, such as $p = 0, q = 5, s = 1$, contribute more to the increase in phase than functions which primarily increase angular correlation, such as $p = 0, q = 1, s = 4$. In the same way that the wavefunction calculated by Roothaan and Weiss (1960) suggests that $\text{H}^-$ is composed of an electron bound weakly to the field of a polarised H atom (Berry 1969), these calculations indicate that this resonance (if it exists) consists of an electron bound weakly to the
polarised core of the model H\textsuperscript{-}. (More recent calculations (Rehmus et al 1978) show that this picture is valid only for a part of the range of distance \(r_1\) of electron 1 from the nucleus.) Such a resonance should not occur below the detachment threshold in electron–H\textsuperscript{-} scattering, but might appear at or just above it.

The consistent appearance of changes of sign in the slope of \(\Delta_0(-), \Delta_0(+)\) and \(\Delta_1(-)\) seems to indicate that the detachment energy for the model potential is approximately 0.048 au, a little less than twice that for H\textsuperscript{-}. Perhaps surprisingly, this agrees best with the estimate of 0.053 au obtained (Valley 1977) by assuming that the correlation energy for the model potential is the same as for Kestner and Sinanoglu’s model.

Calculation of phaseshifts for the approximate polarisation potentials described in §3 were usually done with the basis set (14, 0, 0) which has nine basis functions for \(L = 0\), and eight for \(L = 1\). (These calculations do not contain correlated basis functions.) The convergence of the phaseshifts as a function of basis set size is similar to that for the zeroth-order BG phaseshifts; so additional functions should not change the phaseshifts appreciably. On the other hand, the phaseshifts for the approximate polarisation potentials are as sensitive to variations in \(\zeta\) as the first-order BG calculations. Therefore, it seems that the sensitivity to \(\zeta\) is due to the long-range polarisation potential, while the poor convergence in the basis set size of the first-order calculations is due to correlation effects, especially above the detachment threshold.

The calculations for the first-order adiabatic polarisation potential (equation (15)) use the values of \(\alpha_1 = 23.1\) au and \(\alpha_2 = 260\) au (Valley 1977). The phaseshifts for this potential for \(L = 0\) are given in table 5 and figure 6 and for \(L = 1\) in table 6 and figure 7.

It is obvious from figure 6 that for \(L = 0\), this adiabatic polarisation potential overestimates the phaseshift by almost an order of magnitude at higher energies. On the other hand, the first-order phase is larger than the adiabatic phase for low energies. For \(L = 1\) the adiabatic potential again overestimates the phase for higher energies, although not by an order of magnitude. For low energies, the adiabatic phase is still larger than the first-order phase although they are quite close.

| Table 5. S phaseshifts for approximate polarisation potentials: phase = \(\pi\). |
|---|---|---|---|---|
| \(E_k = \frac{1}{2} k^2\) (Hartree) | Potential | \(V_{\text{ad}}^{(1)}\) | \(V_{\text{pol}}^\omega\) | \(V_{\text{pol}}^{\text{Bock}}\) | \(V_{\text{pol}}^{\infty}\) |
| | | \(\alpha_1 = 23.1\) | \(\alpha_1(0) = 23.1\) | \(\Delta = 0.6\) | \(\beta_1 = 40\) |
| 0.01125 | 0.118 \times 10^{-5} | 0.00023 |
| 0.2 | 0.0002148 | 0.001313 |
| 0.03125 | 0.001275 | 0.001988 |
| 0.03645 | 0.003903 | 0.003335 | 0.003878 | 0.003807 |
| 0.045 | 0.00916 | 0.006416 | 0.01786 | 0.01715 |
| 0.06125 | 0.01848 | 0.01158 |
| 0.08 | 0.01848 | 0.01158 |
| 0.0882 | 0.02358 | 0.01222 |
| 0.09245 | 0.03258 | 0.01328 |
| 0.10125 | 0.03258 | 0.01328 |
| 0.11045 | 0.04975 | 0.01252 | 0.04027 | 0.04222 |
| 0.125 | 0.07158 |
| 0.18 | 0.03738 |
Table 6. P phaseshifts for approximate polarisation potentials.

<table>
<thead>
<tr>
<th>$E_k = \frac{1}{2}k^2$ (Hartree)</th>
<th>$V_{\text{ad}}^{(1)}$</th>
<th>$V_{\text{pol}}^{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_1 = 23.1$</td>
<td>$\alpha_1(0) = 23.1$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_2 = 260$</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>$0.13 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>$0.32 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>0.045</td>
<td>$0.00292$</td>
<td>$0.00109$</td>
</tr>
<tr>
<td>0.06125</td>
<td>$0.00693$</td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td>$0.01158$</td>
<td>$0.00591$</td>
</tr>
<tr>
<td>0.125</td>
<td>$0.0338$</td>
<td>$0.0235$</td>
</tr>
</tbody>
</table>

The $L = 0$ phaseshifts for the second-order adiabatic polarisation potential, $V_{\text{pol}}^{20}$ (equation (20)) and for the non-adiabatic polarisation potential $V_{\text{pol}}^{\text{Buck}}$ (equation (22)) are given in tables 5 and 7. Three sets of $(\beta_1, \Delta)$ values were used in these calculations. Jhanwar and Khare (1975) define $\Delta$ as the effective excitation energy, which is related to $\alpha_1$ by the closure relation

$$\alpha_1 = 4 \left( \psi_0 \sum_i z_i^2 \psi_0 \right) \Delta^{-1}. \quad (36)$$

They also give the relation

$$\beta_1 = \alpha_1 / \Delta \quad (36)$$
Electron scattering by a model negative ion

Table 7. S phaseshifts for approximate polarisation potentials: phase $-\pi$.

<table>
<thead>
<tr>
<th>$E_k = \frac{1}{2}k^2$ (Hartree)</th>
<th>Potential</th>
<th>$\alpha_1 = 23.1$, $\alpha_2 = 260$</th>
<th>$\alpha_1 = 90$, $\alpha_2 = 1800$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{pol}^{\infty}$</td>
<td>$V_{Buck}^{\infty}$</td>
<td>$V_{pol}^{\infty}$</td>
<td>$V_{Buck}^{\infty}$</td>
</tr>
<tr>
<td>$\beta_1 = 110$</td>
<td>$\Delta = 0.2$</td>
<td>$\beta_1 = 900$</td>
<td>$\Delta = 0.1$</td>
</tr>
<tr>
<td>0.03125</td>
<td>0.003664</td>
<td>0.003837</td>
<td>0.01273</td>
</tr>
</tbody>
</table>

which follows from the definitions of $\alpha_1$ and $\beta_1$ if we take $\Delta = 2E_D$, where $E_D$ is the detachment energy. For the first set of ($\beta_1$, $\Delta$) we use $\alpha_1 = 23.1$ au and evaluate equation (35) to obtain $\Delta = 0.6$ au; then equation (36) gives $\beta_1 = 40$ au. For the second and third sets we take $\Delta = 2E_D$ and use equation (36) to obtain $\beta_1$. For the second set, we use $E_D \sim 0.1$ au; this gives $\Delta = 0.2$ au and $\beta_1 = 110$ au. The third set uses $E_D \sim 0.05$ au (as suggested by the BG calculations). Using Adelman’s formulae (equations (18) and (21), Adelman 1972), this value of $E_D$ gives $\alpha_1 = 90$ au and $\alpha_2 = 1800$ au. Taking $\Delta$ to be 0.1 au gives $\beta_1 = 900$ au. The results indicate that, for all three sets of ($\beta_1$, $\Delta$), these two potentials are incapable of correcting the difference between the phaseshift for the adiabatic polarisation potential and the first-order BG phaseshift. Although both potentials decrease the phaseshift, at higher energies ($E_k > 0.08$ au) the decrease is not large enough, and at lower energies ($E_k < 0.045$ au) the adiabatic phaseshift is already too low.

The last approximate polarisation potential we used to calculate phaseshifts is the frequency-averaged polarisation potential defined by equations (24) to (28). The average dipole polarisability, $\langle \alpha_1(\omega) \rangle$, is calculated by substituting Adelman’s formula for $\alpha_1(\omega)$ (equation (31), Adelman 1972) in equation (24). The values of $\langle \alpha_1(\omega) \rangle$ as a function of $\lambda$ are given in table 8 for $\alpha_1(0) = 23.1$ au and for $\alpha_1(0) = 90$ au. At higher energies, the quadrupole term is larger than the averaged dipole term and so should be averaged also. Since $\alpha_2(\omega)$ is not available in a convenient analytical form, $\alpha_2$ has been scaled in accordance with $\langle \alpha_1(\omega) \rangle$ by using Adelman’s equation (21) (Adelman 1972). The phaseshifts for this approximate polarisation potential with $\alpha_1(0) = 23.1$ au are given in table 5 and figure 6 for $L = 0$ and in table 6 and figure 7 for $L = 1$. For $L = 0$ this approximation decreases the phaseshift to the correct order of magnitude for $E_k > 0.08$ au. At low energies, $E_k < 0.045$ au the phaseshift is slightly greater than the adiabatic phase, although both are less than the first-order BG phase. For $L = 1$, the phaseshifts for the frequency-averaged polarisation potential and the phaseshifts for the first-order BG theory agree fairly well. In the case of both $L = 0$ and $L = 1$, the phaseshifts for the approximate polarisation potential are expected to be larger above the detachment threshold than those for the first-order BG calculation because the latter is able to include some of the effect of coupling to the detachment channel. The effect of frequency averaging the polarisability is small for $L > 1$, so calculations based on the static polarisability constants should be sufficient for the energy range considered here.

A few results for a frequency-averaged polarisation potential based on $\alpha_1(0) = 90$ au are given in table 7. The agreement is surprisingly good for $E_k = 0.03125$ au and
0.045 au and, based on the value of \( \langle \alpha_1(\omega) \rangle \) for \( E_k = 0.08 \) au, should also be reasonable for this energy. This agreement supports the assumption that the detachment energy for the model potential is approximately 0.05 au.

Table 8. Frequency-averaged polarisability: \( \langle \alpha(\omega) \rangle \) for \( E(t) = 1/(a^2 + k^2 t^2) \); \( a = (l + \frac{1}{2})/k \).

<table>
<thead>
<tr>
<th>( k )</th>
<th>( \alpha_1(0) = 23.1 ) au</th>
<th>( \alpha_1(0) = 90 ) au</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l = 0 )</td>
<td>( l = 1 )</td>
<td>( l = 0 )</td>
</tr>
<tr>
<td>0.0001</td>
<td>23.10 23.10 90.00 90.00</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>23.10 23.10 92.29 91.06</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>23.10 23.10 92.29 91.06</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>23.14 23.14 92.29 91.06</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>23.48 23.48 98.10 91.06</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>24.91 23.30 92.29 91.06</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>25.24 23.83 71.84 91.06</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>23.19 24.74 52.24 94.08</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>19.92 25.37 37.54 83.38</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>16.53 25.20 27.22 70.96</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>13.51 24.20 20.07 59.18</td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>10.99 22.61 15.09 48.95</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>8.96  20.70 11.58 40.44</td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>6.05  16.77  7.27  27.84</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>4.20  13.28  4.93  19.59</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>3.01  10.47  3.51  14.14</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>2.23  8.28  2.54  10.50</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.70  6.60  1.78  8.02</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. S phaseshifts for McDowell's (1968) polarisation potential: \( \bigcirc \), McDowell; \( \triangle \), model potential.
These calculations indicate that, for scattering from the model potential negative ion, a first-order adiabatic polarisation potential overestimates the S-wave phaseshifts by an order of magnitude at energies greater than the detachment energy. A potential with the second-order adiabatic correction, \(3\beta_1/r^6\), or an energy-dependent potential of the type proposed by Jhanwar and Khare (1975) does not remove the discrepancy in phaseshifts. It appears that the low values of the first-order Bethe–Goldstone phaseshifts are related to the frequency dependence of the polarisability, which is implicitly accounted for in the Bethe–Goldstone calculations.

One of the interesting features of the frequency-averaged dipole polarisability is that for a range of energies less than the detachment energy, the value of \(\langle \alpha_1(\omega) \rangle\) is greater than \(\alpha_1(0)\). If one takes the detachment energy for the model potential to be 0.05 au, this effect occurs at very low energies and the calculations have not yet established whether this behaviour is realistic.

Although the magnitude and energy dependence of these effects would depend on the specific model used, the qualitative results should apply to electron scattering from H⁻. Figure 8 illustrates that, if the same polarisation potential as that used by McDowell (1968) is used in a model potential calculation, results similar to McDowell's are obtained. It therefore appears that the qualitative results of the model potential calculations should be applicable to H⁻.

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