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Phaseshift in the case of scattering from a spherically symmetric potential: connection with valence state parameters

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Abstract

It is shown that the behaviour of the phaseshift describing the scattering of the electron with a certain value of the orbital quantum number l from a structureless potential of a finite action radius at small energies is determined, to high precision, by the energy ε_b and the mean radius r_b of the highest bound state with the same l value in this potential. The exactness of this relation increases as the ε_b value decreases. In the case of long-range potentials, a part of the total phaseshift caused by the scattering from an inner part of the potential, localized within a sphere, is also determined by values of ε_b and r_b characterizing the inner potential. A scheme for determining the parameters ε_b and r_b by using experimental information on the phaseshift is proposed.

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1. Introduction

The behaviour of phaseshifts in the case of scattering from spherically symmetric potentials was investigated actively in the 1930s and 1940s (see references in Mott and Massey (1965)). One of the basic results obtained at that time is a two-parameter representation of the scattering phaseshift at small energies. It was found that, if potentials decrease rapidly enough as the distance between the scattered electron and a target increases, and if shape resonances are absent, the dependence of the phaseshift δ_l on the wavenumber k can be written as

$$k^{2l+1} \cot \delta_l = -1/a_l + 0.5r_l k^2 + O(k^4). \quad (1)$$

This representation is adduced in all standard manuals of scattering theory and is often used in applied research. The two parameters entering in (1), the scattering length a_l and the effective radius r_l , are integral characteristics of the scattering potential and determine completely the phaseshift at small k values. Obviously, under such conditions a shape of the potential describing interactions between the scattered electron and a target is not essential for the behaviour of δ_l . This fact can be easily explained because, in the case when the

wavelength λ of the electron is much greater than the target size, the details of the potential are indistinguishable for the electron.

The important question is whether the scattering parameters a_l and r_l from (1) can be related to quantum-chemical parameters of atomic potentials by means of which chemical bindings in many-atom systems are described (we imply energies of valence states and so on). This question was partially clarified in the same research in the 1930s and 1940s. In particular, it was shown that, if in a target there is a bound s state with a small energy ε_b , the parameters a_l and r_l with $l = 0$ can be expressed in terms of ε_b and some integral including the wavefunction u_b of this state:

$$k \cot \delta_l = -\sqrt{\varepsilon_b} + \rho(\varepsilon_b + k^2) + O[(\varepsilon_b + k^2)^2] \quad (2)$$

where $\rho = \int_0^\infty [\exp(-2\sqrt{\varepsilon_b}r) - u_b^2] dr$.

However, it should be noted that the domain of applicability of (1) is rather restricted. The point is, firstly, that this equation is valid only in a region of small k values, although, of course, this region can be extended by including in (1) summands with larger powers of the variable k , but then the corresponding expressions become more cumbersome and, moreover, it is difficult to show some connection between the new coefficients being added and the quantum-chemical parameters of the potential. Evidently, it should also be emphasized that the expansion of the phaseshift, a smooth function in the case of non-resonance scattering, into a series in terms of k^{2n} , which abruptly increase beginning with $n = 2$, is ineffective. The second restriction to the applicability of (1) arises if there is a shape resonance in the scattering at small energies. In this case the power series (1) becomes quite unacceptable.

Nevertheless, an idea following from equations (1) and (2) that the phaseshift at small k values is determined by a restricted set of integral parameters of the potential and that these parameters are to be connected somehow with quantum-chemical properties of the target can be developed, in our opinion. Our recent studies of the possibility of constructing intratomic potentials through experimental data regarding shape resonances in many-atom systems (Migal 1999) showed that in the energy interval from 0 to 2 Ryd, which is typical for resonance scattering and much wider than the domain of applicability of (1), characteristics of the scattering from separate atoms of a system are determined, exactly enough, by two integral quantities. In particular, in Migal (1999) it has been shown that, in the case of the model muffin-tin (MT) potential (i.e. the potential localized within spheres surrounding separate atoms), such parameters are either the energy ε_b and the mean radius $r_b(\equiv \langle r \rangle)$ of the highest bound state or the energy ε_{res} and the lifetime τ of the resonant state, if such states are in the atomic potential under consideration. (Instead of τ one can employ the half-width γ of the spectral maximum corresponding to the resonance.)

We expect that such a result can be extended to more general classes of potentials. Then, based on this result, it would be possible to work out a new approach, realizable in practice, for solving the inverse problem in the theory of elastic scattering of electrons by atoms and molecules. Within this approach, instead of information about phaseshifts in the whole energy interval from zero to infinity, required in the standard scattering theory, we could restrict ourselves to experimental data of scattering in a limited and most informative interval of small energies. In this case, losing the possibility of constructing an exact potential, we should have gained the possibility of determining the most important quantum-chemical parameters of the potential. This problem will be discussed below.

In this paper, we try to generalize results, obtained in Migal (1999) for specific MT potentials, and determine the domain of applicability of the approach proposed. In particular, the energy interval will be estimated within which the representation of the phaseshift through two quantum-chemical parameters is valid. Also, long-range potentials with Coulomb

asymptotics will be considered. We suppose that, along with the analysis of the relation between scattering characteristics and quantum-chemical parameters of scattering systems, our study can be useful for the development of models of potentials, describing the interaction 'electron + target', and for solving problems related to constructing potentials directly by using experiments of various kinds.

2. Dependence of phaseshift on quantum-chemical parameters

Let us start from the well-known facts relating to the elastic electron scattering from a structureless potential of atomic type. Speaking of an atomic-like potential, we mean a smooth attractive potential which can have a jump only at the outer boundary and absolute values of which do not increase as the radial coordinate r increases (i.e., the model of a square well is admissible). First, let us suppose that the potential has a finite action radius R : $V(r > R) = 0$. Below we accept the R magnitude to be of the order of 1 au, i.e., of the usual atomic size. In the case of short-range potentials the phaseshift δ_l is defined via the asymptotic ($r \rightarrow \infty$) representation of the scattering solution (see, e.g., Mott and Massey (1965))

$$\Psi_l(E, r) \rightarrow \sin(kr - l\pi/2 + \delta_l)/r. \quad (3)$$

If at small energies there are no shape resonances, the behaviour of $\delta_l(E)$ is smooth and conditioned, above all, by the presence of a bound state with a small negative energy in the potential V . We shall assume the presence of such a state. For investigating the character of the above dependence let us consider a complex function F_l which has been introduced in Migal (1999) and can be written as

$$F_l = k^{2l+1}(1 + i\text{ctg}\delta_l) = k^{2l+1}\{1 + i[n_l, R_l]/[j_l, R_l]\} = k^{2l+1}[h_l^{(+)}, R_l]/[j_l, R_l] \quad (4)$$

where R_l is a regular solution of the Schrödinger equation in the region $r < R$, j_l and n_l are the spherical Bessel and Neuman functions, respectively, $h_l^{(\pm)} = j_l \pm in_l$ are the spherical Hankel functions (Abramowitz and Stegun 1970) and $[f_l, R_l]$ are Wronskians calculated for the point $r = R$. The function F_l is related to the scattering matrix S by

$$S_l = -k^{2l+1}[h_l^{(-)}, R_l] \cdot [j_l, R_l]/F_l. \quad (5)$$

From (5) it follows that zeros of the function F_l coincide with poles of the S matrix. It signifies that energies of bound and quasi-bound states are roots of F_l .

Figure 1 shows the behaviour of the function F_l with $l = 0$ for various potentials having bound s states with the same energy $\varepsilon_b = -0.1$ Ryd. Phaseshifts and the corresponding potentials are represented in figures 2 and 3. Obviously, the dependence $F_l(E)$ is sufficiently smooth. This function passes through zero at the energy ε_b of the bound state, and its inclination at this point is determined uniquely by a value of the mean radius r_b of the bound state. (The last statement, concerning the inclination of F_l , is not quite obvious from figure 1, but it is confirmed by a tabular representation.) We can see that the behaviour of the functions F_l and δ_l in a wide energy interval does not depend on any details of the potential except the quantities ε_b and r_b . This fact, possibly, is somewhat unexpected because it does not follow from known theories describing the scattering from spherically symmetric potentials. But it is verified by numerous calculations for various atomic-like models and valid for arbitrary values of l . (Of course, the dependence of scattering properties of the potential on the energy of the bound state is not a surprise. But the fact that, along with the energy, the mean radius of this state determines uniquely the behaviour of the phaseshift in a wide energy interval is unexpected.)

For the function F_l shown in figure 1 it is natural to expect a monotone behaviour in a small energy interval as compared with the distance between the neighbouring roots of F_l . As long

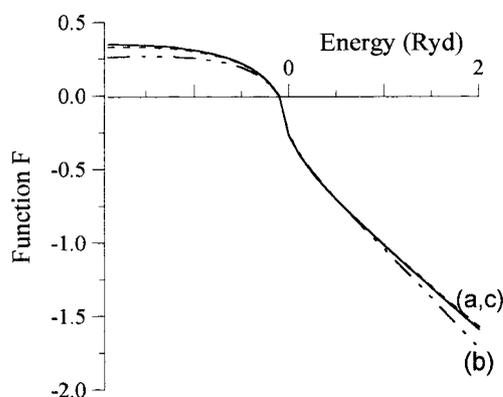


Figure 1. The dependence of the quantity $[(\text{Re } F_l)^2 + (\text{Im } F_l)^2]^{1/2}$ with $l = 0$ on the energy of the scattered electron for potentials with finite action radii and the same energy of bound states $\varepsilon_b = -0.1$ Ryd. Curve a corresponds to a square well with $V = -3.161$ Ryd, $R = 1$ au, $r_b = 2.08$ au, curve b to a square well with $V = -2.302$ Ryd, $R = 1.2$ au, $r_b = 2.18$ au, and curve c to the modified Yukawa potential $(-2.000 - 2.055r^2) \exp(-r)/r$ Ryd with $R = 1.2$ au, $r_b = 2.08$ au. Curves a and c practically coincide.

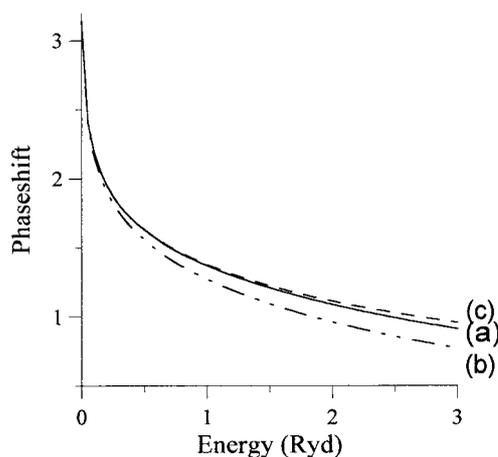


Figure 2. The phaseshifts with $l = 0$ for the same potentials as in figure 1. Curves a and c practically coincide in the interval from 0 to 2 Ryd.

as the distance between energies of neighbouring bound or quasi-bound states with a given l value is some tens of rydbergs for atomic potentials interrupted at $R \sim 1$ au, then the interval of the monotone behaviour of F_l is expected to be of the order of some rydbergs. We can assume that it is the interval within which the complex functional dependence of the phaseshift on the potential is reduced, on the whole, to a dependence only on the two parameters ε_b and r_b . Below we shall return to this question and give examples confirming the last statement.

The fact that, in a wide enough interval of energies, δ_l apparently depends only on the two parameters, should be interpreted. In particular, it would be interesting to consider how the wavefunctions behave in the case of two different potentials having bound states with the same values of ε_b and r_b . Figure 4 shows radial parts of the wavefunctions ψ_l calculated for the potentials V_a and V_c from figure 3. At the beginning let us consider the functions of bound

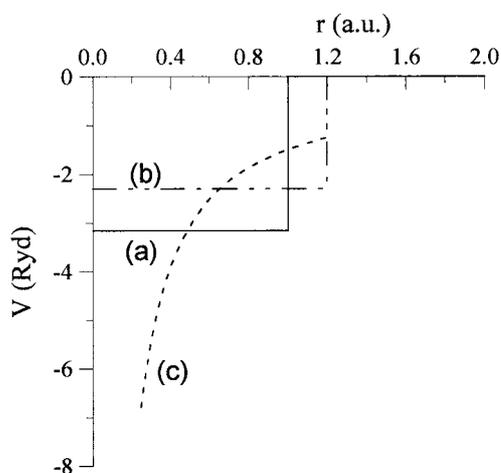


Figure 3. Model potentials used for calculations of the function F_l and the phaseshifts shown in figures 1 and 2. Curve a corresponds to a square well with $V = -3.161$ Ryd, $R = 1$ au, $r_b = 2.08$ au, curve b to a square well with $V = -2.302$ Ryd, $R = 1.2$ au, $r_b = 2.18$ au, and curve c to the modified Yukawa potential $(-2.000 - 2.055r^2) \exp(-r)/r$ Ryd with $R = 1.2$ au, $r_b = 2.08$ au.

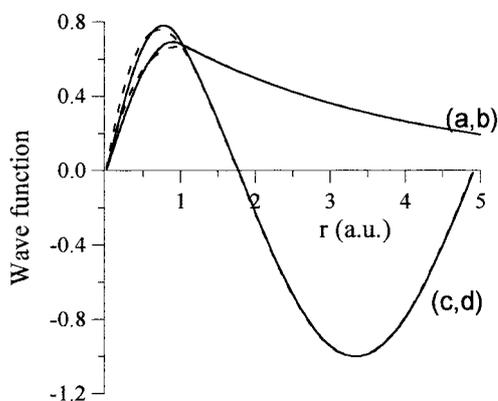


Figure 4. Radial parts of the wavefunctions with $l = 0$ for potentials a and c from figure 3. The full curves correspond to potential a, the broken curves to potential c. Curves a and b are for the functions of bound states with $\varepsilon_b = -0.1$ Ryd and $r_b = 2.08$ au, curves c and d are for the functions of the continuum spectrum with $E = 1$ Ryd.

states. We can see immediately that these functions are close enough. Notice that in the region $r > R$ they just coincide. Yet in the region $r < R$, where one of the potentials is deeper, the corresponding wavefunction must change more rapidly. Therefore, for instance, as r increases, the function ψ_c at first increases more rapidly than ψ_a , but after the point $r = 0.5$ au, where V_a is deeper than V_c , conversely ψ_c increases more slowly than ψ_a . At the exit from the potential, at the point $r = R$, the logarithmic derivatives of both functions must be equal because in the region $r > R$, where $V = 0$, both functions are proportional to the same function $h_l^{(+)}(ikr)$. The distinction is possible only for normalizing coefficients. At small modulo energies ε_b , when the wavefunctions of bound states are delocalized sufficiently and mean radii exceed the

R values, the distinctions between ψ_i at inner points are not essential, and the normalizing coefficients become very close to each other. Obviously, the lower the $|\varepsilon_b|$ value and the greater r_b , the less the distinction between the normalizing coefficients. Then values of the wavefunctions in the outer region must be practically identical.

In the case of small positive energies E the behaviour of the wavefunctions at inner points is almost similar to the behaviour of the functions of bound states with small $|\varepsilon_b|$. It is most important that substituting the potential V_a by the potential V_c does not change the value of the logarithmic derivative at the point $r = R$. It is this fact that leads, as the final result, to the identity of the phaseshifts δ_l for both potentials. It should be remembered that, in the case of potentials of finite action radius, the values of δ_l are completely determined by values of the logarithmic derivative $L_l(E, r)$ at the point $r = R$ through the relation

$$\tan \delta_l = \frac{j_l(kR)L_l(E, R) - j_l'(kR)}{n_l(kR)L_l(E, R) - n_l'(kR)}. \quad (6)$$

Of course, it is impossible to prove strictly that from the equality of the logarithmic derivatives of the functions of bound states for two different potentials, it follows that the logarithmic derivatives of the wavefunctions at positive energies for the same potentials are equal also. Nevertheless, based on the results of calculations indicating that the function F_l changes monotonically in a wide energy interval and is smooth enough (see figure 1), we can expect that the equality of the logarithmic derivatives is kept as the energy E changes slightly with respect to the energy ε_b of the bound state. Then we can connect directly the behaviour of the phaseshift at small positive energies with values of the parameters ε_b and r_b which are related uniquely to values of the logarithmic derivatives of the wavefunctions of bound states at the point $r = R$. In this way, the parameters ε_b and r_b may be considered as important integral characteristics of the scattering potential.

Having further practical applications as an objective, we need to consider at greater length in what energy interval $\Delta E = E - \varepsilon_b$ the phaseshift is determined completely by the two parameters. From the simplest consideration, based on the smoothness of the function F_l and already mentioned previously, it follows that, above all, the value ΔE must satisfy the relation $\Delta E \ll |\varepsilon_{b,i} - \varepsilon_{b,i+1}| = \Delta\varepsilon_b$ where $\varepsilon_{b,i}$ and $\varepsilon_{b,i+1}$ are neighbouring energy levels in a given potential, and one of which is ε_b . (If in a potential there is only one bound or quasi-bound state, in order to evaluate the magnitude $\Delta\varepsilon_b$ it is necessary first to deepen this potential so that the second similar state appears in it.) Obviously, if one can achieve the coincidence of the values ε_b and r_b corresponding to the highest bound states in two potentials with different forms, it does not quite signify that the energies of the other bound or quasi-bound states in such potentials coincide too. Therefore, although the functions F_l for two different potentials behave identically near a coinciding root, they will behave differently far from this root, approaching distinct roots. Phaseshifts for these potentials will differ noticeably as the energy E moves away from the coinciding root.

To check the proposed estimate of ΔE we performed calculations for potentials which are deeper than those represented in figure 3. From the previous consideration it follows that the deeper the potentials and the greater the values $|\varepsilon_b|$, the greater the magnitude ΔE , even for the smallest positive energies, and the phaseshifts for two potentials with the same ε_b and r_b become different. Indeed, it was found that as the potentials intensify, the two-parameter dependence of δ_l on ε_b and r_b becomes less exact. In the case of potentials with $\varepsilon_b = 3$ Ryd it is still valid approximately. However, for potentials with $\varepsilon_b = 10$ Ryd the phaseshifts already essentially differ. The distance $\Delta\varepsilon_b$ between the neighbouring levels in these potentials is of the order of 23 Ryd (in the square well with depth $V = -45$ Ryd and $R = 1.2$ au there are two bound states with $\varepsilon_{b1} = -0.68$ Ryd and $\varepsilon_{b2} = -23.8$ Ryd). The phaseshifts and radial

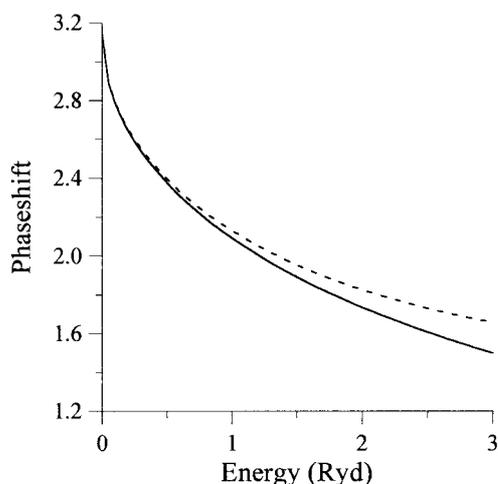


Figure 5. The phaseshifts with $l = 0$ for potentials with $\varepsilon_b = -3.0$ Ryd and $r_b = 0.789$ au. The full curve corresponds to a square well with $V = -7.978$ Ryd, $R = 1$ au, and the dashed curve to the potential $(-2.01 - 5.10r - 6.52r^2) \exp(-r)/r$ Ryd with $R = 1.2$ au.

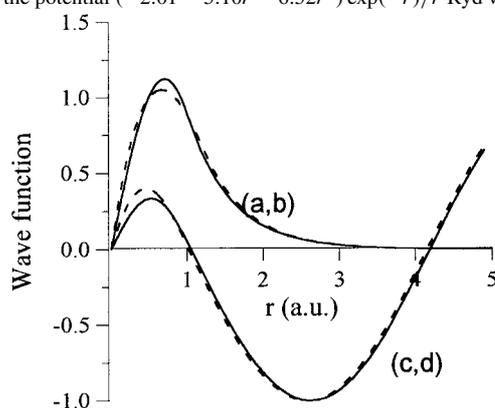


Figure 6. Radial parts of the wavefunctions with $l = 0$ for potentials with $\varepsilon_b = -3.0$ Ryd and $r_b = 0.789$ au. The full curves correspond to a square well with $V = -7.978$ Ryd, $R = 1$ au, and the dashed curves to potential $(-2.01 - 5.10r - 6.52r^2) \exp(-r)/r$ Ryd with $R = 1.2$ au. Curves a and b are for the functions of bound states, curves c and d are for the functions of the continuum spectrum with $E = 1$ Ryd.

parts of the wavefunctions for the potentials with $\varepsilon_b = 3$ Ryd (when it is still admissible to assume that $\Delta E \ll \Delta\varepsilon_b$) are represented in figures 5 and 6.

3. Two-parameter dependence of phaseshift in the case of the long-range potential

In the previous section, the fact of the presence of a finite action radius of the potential proved to be substantial. However, the dependence of the phaseshift on two parameters, similar to the one considered above, can exist in the case of long-range potentials too. Let us consider the most important practical case of the Coulomb potential. We suppose that, in the region $r < R \sim 1$ au, the potential has a form similar to that studied in the previous section, and in the region $r > R$ the potential is pure Coulomb, $V = -2/r$. A more general case when, along

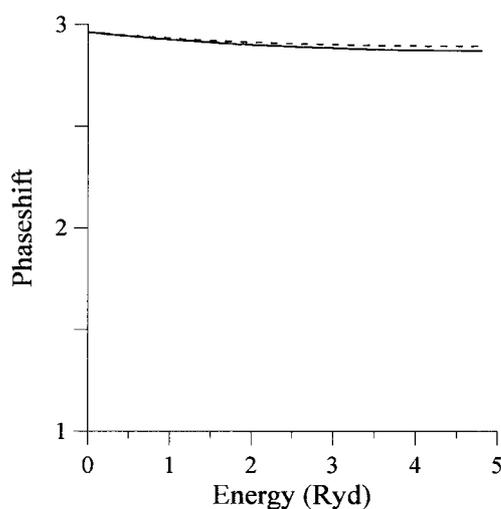


Figure 7. The shifts of the Coulomb phase with $l = 0$ for two potentials with identical outer part $V(r) = -2/r, r > R = 1.0$ au. The full curve corresponds to the inner potential in the form of a square well with $V = -3.161$ Ryd (potential a from figure 3) and the dashed curve to the inner potential $(-0.806 - 6.00r^2) \exp(-0.8r)/r$ Ryd. In both the inner potentials (without taking account of the Coulomb tails) there are bound states with the same parameters $\varepsilon_b = -0.1$ Ryd and $r_b = 2.08$ au.

with the Coulomb, there is some additional potential, decreasing rapidly as r increases, does not change the situation in principle and will be considered below.

At large r values, instead of (3), we now have (see Mott and Massey (1965))

$$\Psi_l(E, r) \rightarrow \sin[kr - \ln(2kr)/k - l\pi/2 - \arg\Gamma(l + 1 + i/k) + \sigma_l]/r. \quad (7)$$

The quantity σ_l entering into (7) plays the role of the phaseshift arising from the deviation of the potential from the Coulomb one. In contrast to the quantity δ_l considered above, the function σ_l at $k \rightarrow 0$ can be equal to an arbitrary value, rather than to a value divisible by π . The dependence of σ_l on the energy is also a smooth function (if resonances are absent) and, by analogy with the previous section, one can expect that this function is determined by a small number of parameters.

The point is that σ_l satisfies the following equation similar to (6):

$$\tan \sigma_l = \frac{P_l(E, R)L_l(E, R) - P_l'(E, R)}{Q_l(E, R)L_l(E, R) - Q_l'(E, R)} \quad (8)$$

where, instead of the Bessel and Neuman functions, the regular P_l and singular Q_l solutions of the Coulomb type are written. The logarithmic derivative L_l is the only quantity from (8) depending on the potential at inner points (let us call this potential the inner potential). Obviously, $L_l(E, r)$ contains the same information about the inner potential as in the case of the function δ_l . Therefore, it is natural to expect that the quantity σ_l is determined by parameters of a bound state in the inner potential. Undoubtedly, for the potential interrupted at point $r = R$ (without the Coulomb tail) it is possible to introduce notions of the energy and the mean radius of a bound state, and these parameters corresponding to the highest state must determine the behaviour of σ_l .

To illustrate the point stated above, the quantities σ_l calculated for inner potentials with different forms are shown in figure 7. Obviously, the curves corresponding to the dependence σ_l on E in the case of potentials with equal ε_b and r_b coincide in practice up to 3 Ryd.

However, there is some difference between the situations for the potentials of finite action radius considered in the previous section and for distorted Coulomb potentials being studied here. In the first case the R values for various potentials could be different. But in the second case, when an addition to the Coulomb phase is examined, the R values must be identical. Otherwise, the potential of smaller radius should be extended in the domain of the definition of the potential of larger radius by adding the Coulomb potential.

Now let us turn to potentials which are not pure Coulomb outside a sphere of radius R but asymptotically approach it. The previous considerations remain valid, in the main. The distinction is only that, in this case, the Coulomb functions P_l and Q_l from (8) should be substituted by modified functions which, at large r values, coincide with P_l and Q_l but at other points are determined by the numerical integration of the Schrödinger equation with a given potential. In this case the total phaseshift σ_l can be represented as the sum of two summands, $\sigma_l^{(in)} + \sigma_l^{(out)}$, where $\sigma_l^{(in)}$ and $\sigma_l^{(out)}$ are shifts of the Coulomb phase for inner and outer potentials, respectively. Of course, it should then reveal the dependence of the quantity $\sigma_l^{(in)}$ on the parameters of the inner potential.

It is also obvious that, in the case of long-range potentials, as well as in the previous section, the dependence of the phaseshift on the parameters ε_b and r_b is valid only in the energy interval $\Delta E \ll |\varepsilon_{b,i} - \varepsilon_{b,i+1}|$, where $\varepsilon_{b,i}$ and $\varepsilon_{b,i+1}$ are neighbouring energy levels in the interrupted potential.

From the above a curious result follows. Let there be some potential stretched enough, possibly with the Coulomb asymptotics. Without distorting the total scattering phase, we can substitute a part of this potential from some interval $[0, R]$ by another potential, providing that each of these interrupted potentials has a bound state with the same small energy and mean radius. It is easy to see that the smaller the value of R , the wider the energy interval in which the phaseshifts calculated for both potentials must be identical.

4. Determination of parameters of valence states from experiment

In this section we consider how the discovered dependence of the phaseshift on the parameters ε_b and r_b can be used for obtaining information on these parameters from scattering experiments. The fact that, at small energies, a functional dependence $\delta_l[E, V(r)]$ is equivalent to a two-parameter relation $\delta_l(E, \varepsilon_b, r_b)$, allows the phaseshift to be expanded in a basis consisting of two functions, each of them depending only on the energy E . This general argument enables us, in principle, to construct simple relations for δ_l and functions of δ_l which could be useful for deciphering experiments. Unfortunately, we did not succeed in searching for a general expression for expanding the phaseshift by means of analytic transformations. However, a particular expression relating to F_l has been obtained empirically through the consideration of the dependence of F_l on parameters (Migal 1999). It was found that if, for a potential with known values of the parameters ε_b and r_b the dependence $F_l(E)$ is given (we denote it by f_l), then for a potential with altered values of the parameters $\varepsilon_b + \Delta\varepsilon_b$ and $r_b + \Delta r_b$ the function F_l can be represented in the form (below we omit the index l that should always be present)

$$F(E, \varepsilon_b + \Delta\varepsilon_b, r_b + \Delta r_b) = f(E, \varepsilon_b, r_b) + c(\Delta\varepsilon_b)\varphi(E) + d(\Delta r_b)\chi(E). \quad (9)$$

Here $\varphi(E) = F(E, \varepsilon_b + \Delta\varepsilon_b, r_b) - f(E, \varepsilon_b, r_b)$, $\Delta\varepsilon_b$ is a preassigned alteration of ε_b , $\chi(E) = F(E, \varepsilon_b, r_b + \Delta r_b) - f(E, \varepsilon_b, r_b)$, Δr_b is a preassigned alteration of r_b , c and d are real coefficients determined so that $c = 1$ as $\Delta\varepsilon_b = \Delta\varepsilon_b$, and $d = 1$ as $\Delta r_b = \Delta r_b$. Apparently, changes of parameters ε_b and r_b in (9) must not be large. It is also clear that any function of δ_l , including δ_l itself, can be written in a form similar to (9).

We suppose that equation (9), in which the dependence of the phaseshift on the energy and the parameters ε_b and r_b is factorized, can be considered as some mathematical formula realizing the connection between these quantities shown in the previous sections. On the basis of this equation we succeeded in constructing a scheme by means of which the parameters ε_b and r_b can be determined via scattering experiments at small energies. Below we describe the scheme, assuming that a real spectrum is already processed and the dependence $F(E)$ is revealed (we call it the ‘experimental’ function $F_{\text{exp}}(E)$).

Within the framework of the scheme, at the beginning one chooses three auxiliary model potentials with some distinct eigenvalues ε_b and r_b , and for these potentials one calculates functions $F^{(i)}(E)$ ($i = 1, 2, 3$). These functions are linearly independent functions, and one of them should be assumed to be $f(E, \varepsilon_b, r_b)$. The subtraction of the other functions from $f(E, \varepsilon_b, r_b)$ gives us the functions $\varphi(E)$ and $\chi(E)$. Then, supposing that the ‘experimental’ function F_{exp} satisfies (9), one should determine the coefficients c and d from (9) by using any two values of $F_{\text{exp}}(E)$ with $E > 0$. After determining all the functions and coefficients entering into (9) one can continue the dependence $F(E)$ into the domain of negative energies. A root of $F(E)$ within the $E < 0$ domain is just one of the desired parameters, ε_b . Then, by means of any model potential, fitting its parameters so that the energy of the bound state in it is equal to the ε_b value, one determines the eigenfunction $F(E)$ for this potential. By further alteration of the parameters of the potential one obtains that the inclination of the tangent of the function $F(E)$ at the point $E = \varepsilon_b$ coincides with the inclination of the tangent of the function $F_{\text{exp}}(E)$. Under such conditions both the curves, $F(E)$ and $F_{\text{exp}}(E)$, practically coincide in a wide energy interval. Finally, for the model potential constructed one calculates the mean radius r_b of the bound state, and it is the second quantity desired.

This scheme is realized easily, and below we illustrate the application of the scheme to a concrete example. It should be noted that in this paper, in our opinion, it is not necessary to use real experimental shifts of the scattering phase. In order to demonstrate the possibilities of the method proposed it is enough, at first, to consider a model problem. For our analysis we chose the $l = 1$ phaseshift for the Be atom with a vacancy in the K shell, obtained by calculating within the Hartree–Fock approach. In contrast to the models of structureless local potential used in our previous calculations, the potential within this task is of a more general type. It is non-local due to taking account of exchange effects, with the Coulomb asymptotics due to the vacancy in the inner shell, and with a stretched (up to $R \sim 1.5$ au) distortion of the Coulomb field. Our purpose is also to show that the two-parameter approximation (9) for the phaseshift is valid for non-local potentials as well.

The given phase and the phase constructed within the two-parameter approximation are represented in figure 8. Obviously, these phases are close enough. The difference between them is one percent or less, i.e. comparable with the errors of calculations of such quantities. The effective values of the parameters of the potential being studied are determined. In this case these parameters are the energy and the half-width of a resonant state characterizing the interrupted potential. This state turns into a bound state if the Coulomb tail is taken into account. The meaning of the parameters obtained lies in the fact that a structureless local potential with such parameters is completely equivalent to the complex non-local potential under consideration when the elastic scattering of the electron in the considered interval of small energies is investigated.

It should be emphasized that the imitating potential obtained, $V = -4.3/r$ ($r < 1.516$ au), is not unique. One can construct an infinite number of potentials with the same phases, but it is essential that all these potentials with different forms have resonant states with the same values of the energy and half-width.

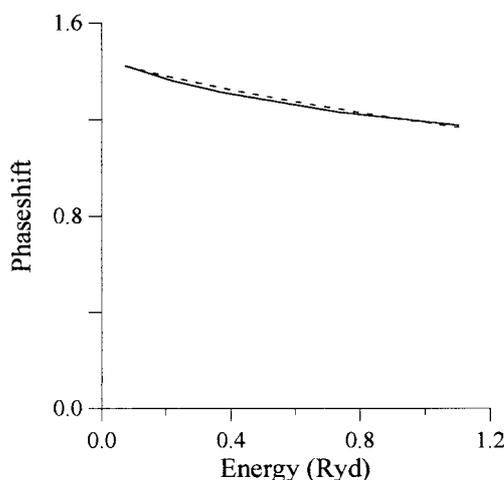


Figure 8. The fitting of the shift of the Coulomb phase with $l = 1$ (the broken curve) to the phaseshift obtained within the Hartree-Fock approach for the beryllium atom in the state $1s^1 2s^2$ (the full curve). The imitating model potential at inner points ($r < R = 1.516$ au) is $V = -4.3/r$, and at outer points ($r > R$) is $V = -2/r$. In the inner potential (without taking account of the Coulomb tail) there is a quasi-bound state with the energy $\varepsilon_{\text{res}} = 0.021$ Ryd and the half-width $\gamma = 0.0028$ Ryd.

5. Conclusions and perspectives

Our research shows that the behaviour of the phaseshift with a certain value of l in the energy interval from 0 to 2 Ryd involves information sufficient for determining the energy and mean radius of the highest bound state with the same value of l in the potential of the target. Speaking about the parameters of the state, we mean not the exact characteristics of this state in an atom, but certain integral characteristics of the potential which can be reproduced within the simplest models. Undoubtedly, if these parameters are obtained empirically, they reflect automatically all details of the real intratomic interactions which prove to be important for such quantities including the effects of reconstructing the structure of the atom, the non-locality of interactions, and so on. We suppose that these parameters are objective characteristics of an atom as a scattering system. Besides, they are visual and have a distinct physical meaning.

An analysis of these parameters could be useful for examining states of atoms in various compounds because these parameters reflect changes of the states of atoms. In particular, within the MT model of a many-atom system the scattering of electrons with positive energies (from 0 to 2 Ryd) by separate atoms of the system can be described completely by means of these parameters (Migal 1998, 1999). This fact allows us to connect peculiarities in scattering from the whole system with the parameters of valence states of separate atoms. Determining from some experiments (e.g. soft x-ray absorption by matter) the dependence of the phaseshifts on the energy for separate atoms, it is possible to find parameters of valence states and observe changes of these states passing from one compound to the other.

Moreover, having information on ε_b and r_b values for separate atoms, one can determine (e.g. within the MT model) values of the energies of valence states of the whole system. Such a direction, apparently, is promising, and we suppose that in this way it would be possible to formulate a new concept of quantum chemistry in which energies and mean radii of valence states could be the basic parameters. In contrast to those quantities often used today for the description of chemical binding (e.g. effective charges of atoms or overlapping integrals in

MO LCAO) which are not determined uniquely from experiment, the energies and mean radii of valence states of separate atoms can be defined reliably via experiment.

The other reasoning of general character regarding quantities ε_b and r_b is related to the inverse problem of the scattering theory. It is well known that for constructing a full potential it is necessary to have an infinite amount of information, including the behaviour of the phaseshift with a given l value in the infinite energy interval. Obviously, in practice this is impossible. The known alternative approaches (see, e.g., Chadan and Sabatier (1977)), where values of phaseshifts with all l values at a fixed energy are required, enable potentials to be constructed non-uniquely. Hence, we can calculate on obtaining only some restricted information on a real potential and determine only a limited number of its characteristics. Our approach allows us to solve the inverse problem partially and to find two integral characteristics of the potential, most important from our point of view, for chemical applications.

It is essential that the energy interval from 0 to 2 Ryd being investigated by us is very informative. Since the behaviour of the phaseshift in this interval is determined, in the main, by the parameters ε_b and r_b , we can suppose that the discovered two-parameter dependence allows us to decipher almost all information from this interval. The investigation of shifts of the scattering phase in a wider interval, must apparently, enlarge the amount of information on the potential and give us its further characteristics. The main problem in this case is to associate a chosen energy interval with the minimum number of characteristics determining the behaviour of the phaseshift in this interval and define these characteristics.

One possible way of revealing such characteristics is as follows. Instead of a two-component expansion (9) one can use the expansion of a given function F_l in N linearly independent functions, $N \geq 3$. Such functions can be functions $F_l^{(i)}$ for any N distinct potentials. For each set of functions one should find the corresponding energy interval in which the expansion of F_l is valid. Then it is necessary to reveal N independent physical parameters x_i determining the dependence $F_l = f(E, x_1, x_2, \dots, x_n)$ on E in the established interval. (Of course, the last step is the most difficult and the most interesting part of the whole task.) Finally, increasing the N value, one could solve the inverse problem more and more completely and determine the new characteristics of the potential.

In conclusion, one can note that the proposed method for analysing phaseshifts can be extended easily to the case of resonance scattering. In this case, for example in expansion (9), instead of parameters ε_b and r_b of bound states one should use parameters ε_{res} and γ of resonant states.

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