

Analytical Representation of Hartree Potentials and Electron Scattering

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Analytical fits to the Hartree curves of 19 neutral atoms are presented. These are in the form of either Wentzel potentials, for lighter elements, or a series of Wentzel-like terms, for heavier elements. Applications to the scattering of electrons by atoms are briefly discussed. Among the principal results is an iteration method which yields expressions, in terms of tabulated integrals, for the radial eigenfunctions for a particle scattered by a Wentzel potential.

INTRODUCTION

THE collision of electrons with atoms is, properly speaking, a many-body problem. As such, it is not easily amenable to exact treatment and recourse to approximation methods is necessary. Regardless of the strength (or weakness) inherent in any approximation used, the results of calculating quantities of interest in scattering applications will be affected, to some extent, by the interaction potential employed. It is, therefore, clearly desirable to have as accurate an analytical approximation to the atomic potential as possible. Of the potential functions proposed, the Hartree potential corresponds to the best approximation of the atomic wave function which can be achieved by regarding it as a product of the one-electron wave functions chosen so as to minimize the value of the total energy, neglecting spin-orbit terms. The purposes of this note are these: (1) to furnish accurate analytical approximations to the Hartree potentials; (2) to discuss briefly some applica-

tions in electron scattering utilizing the expressions we find for the potentials.

The energy domain discussed is nonrelativistic.

REPRESENTATION OF THE HARTREE POTENTIALS

The interaction potential, based on the Hartree scheme, may be written

$$V(r) = (-Ze^2/r)(Z_p/Z). \quad (1)$$

The Coulomb potential of the nucleus is modified by the factor Z_p/Z , representing the screening effect of the orbital electrons on the nucleus. The function Z_p/Z satisfies the conditions $Z_p/Z \rightarrow 1$ as $r \rightarrow 0$; $Z_p/Z \rightarrow 0$ as $r \rightarrow \infty$. Tabulated numerical values of the quantity Z_p/Z exist for a number of atoms and ions.^{1,2} We wish to represent them analytically. To do this, semilogarithmic plots of Z_p/Z as a function of $x = 1.13Z^{1/3}r/a_0$, the Thomas-Fermi variable, are useful. Here, and throughout, the quantity a_0 is the Bohr radius of hydrogen. Figure 1 shows a plot of Z_p/Z versus x for a few elements, with the Thomas-Fermi screening factor, $\Phi(x)$, included for comparison. There is, as seen, a difference between the Thomas-Fermi and Hartree representations which becomes large as the atomic number Z decreases. This reflects a breakdown of the statistical model of the atom on which the Thomas-Fermi potential is based. For the Hartree functions, the Z_p/Z curves deviate but little from linearity in several cases. This means that they can be fit, when a linear plot exists, with one term of the form $Z_p/Z = e^{-bx}$, where b is a constant to be determined. The potential will then be a Wentzel type. For heavier elements, Ruark³ first proposed the representation

$$Z_p/Z = \sum_n c_n e^{-b_n x}. \quad (2)$$

$\sum_n c_n = 1$, but otherwise, the c_n and the b_n are adjustable. We have found that by making some of the c_n negative, it is possible to account for the localization of charge due to electron shells; this is manifested by slight sinuities in the Z_p/Z curves.

Table I contains the results of fitting 19 Hartree curves of neutral atoms, ranging in atomic number from

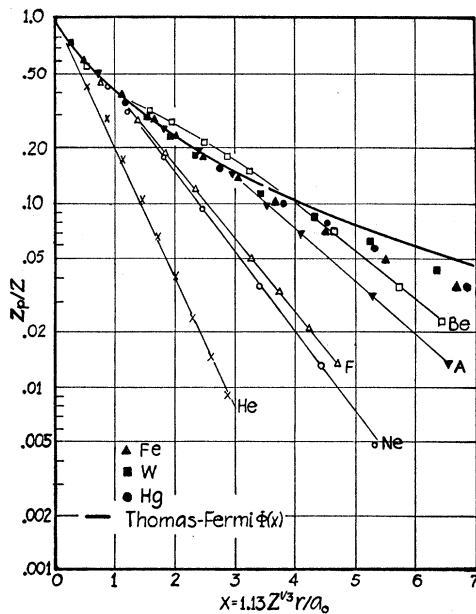


FIG. 1. Screening factors, Z_p/Z , as a function of the variable $x = 1.13Z^{1/3}r/a_0$, for selected atomic numbers.

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¹ A. J. Freeman, Phys. Rev. **91**, 1410 (1953).

² D. R. Hartree, *Reports on Progress in Physics* (The Physical Society, London, 1946), Vol. 11, p. 113.

³ A. E. Ruark, Phys. Rev. **57**, 62 (1940).

$Z=2$ to $Z=80$ by either one-term Wentzel potentials or series of the form of Eq. (2). The Thomas-Fermi function is given by a representation due to Molière.⁴ The series for the Hartree curves are accurate, generally, to within about 5% out to a distance at which Z_p/Z has fallen to a value of about 0.01. Some are considerably more accurate. The potentials for A and Kr contain a polarization correction after the fashion of Holtzmark.⁵

For ions, a series of the form

$$Z_p/Z = \pm n/Z + [(Z \mp n)/Z] \{ \sum_k c_k e^{-b_k x} \}, \quad (3)$$

where n is the numerical value of the charge on the atomic ion, yields accurate results.

APPLICATIONS

If one now substitutes the analytical fits to the potentials into a first Born approximation, there results for the scattering cross section $I(\theta)$

$$I(\theta) = (2mZe^2/\hbar^2)^2 \{ \sum_n c_n / (K^2 + d_n^2) \}^2, \quad (4)$$

where $K = (2p_0 \sin \frac{1}{2} \theta) / \hbar$, and $d_n = b_n (1.13Z^{1/3} a_0^{-1})$. In these formulas, p_0 is the initial momentum of the electron, and θ is the angle of scattering in the center-of-mass coordinate system. It has been found that when potentials containing polarization corrections are used in (4), the agreement between calculated and observed cross sections is, as expected, better at small scattering angles than cross sections found by neglecting polarization entirely. For the remainder of the cross sections we have computed using (4), the errors are those inherent in the Born approximation. That is, the Born approximation yields a monotonically decreasing cross section for all incident electron velocities and all atomic numbers. The strong backscattering and diffraction patterns sometimes observed experimentally cannot be predicted by the Born approximation.⁶

When the Born approximation is no longer useful, phase shift methods are usually employed to find accurate values for the scattering cross section. The use of the potentials in finding phase shifts is illustrated below, using a variational principle due to Pais.⁷ The method is unsuited for the determination of zero-order phase shifts. The Pais principle can be formulated in the following way. If, in the radial wave equation $Lw_n = 0$, with L the operator

$$L = \frac{d^2}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} - U(r) \right],$$

one makes the assumption that $U(r) \ll n(n+1)/r^2$, then the potential may be treated as a perturbation on the

angular momentum of the particle. One then assumes that the effect of the potential is to produce a phase shift which is found mathematically as a shift in the index of the Bessel function characterizing the free particle solution. Thus, one takes w_n to be of the form

$$w_n(r) = J_{n+\frac{1}{2}+\Delta n}(kr). \quad (5)$$

The boundary conditions satisfied by this function are

$$w_n(0) = 0; \quad \lim_{r \rightarrow \infty} w_n(r) \sim \sin(kr + n\pi/2 + \Delta n\pi/2).$$

Since the latter condition is characteristic of the asymptotic form of the wave function in scattering problems, the phase shifts produced by the potential may be related to the Δn through the equation

$$\delta_n = -\pi \Delta n / 2. \quad (6)$$

The Δn are now fixed by requiring that

$$\int_0^\infty w_n L w_n dr = 0. \quad (7)$$

If (5) is placed into (7), the result is, for potentials given by Eq. (2),

$$\frac{\Delta n(\Delta n + 2n + 1)}{2\Delta n + 2n + 1} = \frac{mZe^2}{\hbar^2 k} \sum_t c_t Q_{n+\Delta n}(1 + d_t^2/2k^2), \quad (8)$$

TABLE I. Exponential fits of Z_p/Z and of the Thomas-Fermi $\Phi(x)$.

Element	Z_p/Z (one term)	Z_p/Z (series of terms) ^a
* He	$e^{-1.60x}$	$1.25e^{-1.75x} - 0.25e^{-3.846x}$
Be		$e^{-0.574x} - 0.48e^{-1.081x} + 0.48e^{-3.06x}$
C		$1.25e^{-0.828x} - 0.44e^{-1.41x} + 0.19e^{-4.29x}$
N	$e^{-0.95x}$	$1.20e^{-0.904x} - 0.32e^{-1.43x} + 0.12e^{-9.65x}$
O	$e^{-0.919x}$	$1.25e^{-0.991x} - 0.35e^{-1.63x} + 0.10e^{-18.3x}$
F	$e^{-0.907x}$	
Ne	$e^{-0.978x}$	
A		$[0.84e^{-0.566x} - 0.24e^{-1.056x} + 0.40e^{-3.25x}]^a$
		$0.659e^{-0.574x} + 0.341e^{-2.77x}$ (Ruark ^b)
K		$0.124e^{-0.0514x} + 0.68e^{-0.765x} + 0.196e^{-2.80x}$
Ca		$0.20e^{-0.195x} + 0.56e^{-0.770x} + 0.24e^{-3.08x}$
Cr	$e^{-0.781x}$	$e^{-0.781x} - 0.20e^{-1.26x} + 0.20e^{-3.70x}$
Fe		$0.25e^{-0.335x} + 0.56e^{-0.828x} + 0.19e^{-3.76x}$
Zn		$0.22e^{-0.319x} + 0.78e^{-1.081x}$
Ge		$0.22e^{-0.263x} + 0.78e^{-1.165x}$
As		$0.295e^{-0.387x} + 0.705e^{-1.295x}$
Br		$0.360e^{-0.366x} + 0.640e^{-1.483x}$
Kr		$[0.335e^{-0.290x} + 0.60e^{-1.33x} + 0.065e^{-7x}]^a$
		$0.415e^{-0.378x} + 0.51e^{-1.48x} + 0.075e^{-7x}$
W		$0.19e^{-0.216x} + 0.72e^{-0.970x} + 0.09e^{-15x}$
Hg		$0.19e^{-0.257x} + 0.56e^{-0.779x} + 0.25e^{-3.16x}$
$\Phi(x)$		$0.35e^{-0.3x} + 0.55e^{-1.2x} + 0.1e^{-6x}$

^a The expressions in square brackets contain a polarization correction (reference 5).

^b See reference 3.

⁴ G. Molière, Z. Naturforsch. 2a, 133 (1947).

⁵ J. Holtzmark, Z. Physik 55, 437 (1929); 66, 49 (1930).

⁶ For an excellent review of electron scattering, see the review article by J. H. McMillen, Revs. Modern Phys. 11, 84 (1939).

⁷ A. Pais, Proc. Cambridge Phil. Soc. 42, 45 (1946).

TABLE II. Phase shifts in helium.

Voltage	Phase (radians)	Approximation Pais	Exact McDougall	Approximation Born
16	δ_1	0.067	0.070	0.042
	δ_2	0.0069	0.0065	0.0045
25	δ_1	0.1139		
	δ_2	0.0130		
49	δ_1	0.170	0.186	0.148
	δ_2	0.042	0.0411	0.0329
	δ_3	0.0101		
121	δ_1	0.249	0.272	0.224
	δ_2	0.0896	0.0946	0.0769
	δ_3	0.0396		
340	δ_1	0.272	0.308	0.274
	δ_2	0.1389	0.1524	0.1379

where the $Q_{n+\Delta n}$ are Legendre polynomials of the second kind. Equation (8) is a transcendental one in the Δn . Application of (8) to the case of scattering of electrons by He for incident electron energies in the voltage range $16 \leq V \leq 340$ yields phase shifts which are significantly better than Born phases. Comparison is made with the exact work of McDougall.⁸ At the higher energies, the Pais and Born calculations are equivalent. Table II presents the results.

To deal with the question of zero-order phase shifts, where the Pais principle cannot be applied, it is possible to use other variational principles which are related to the Pais method. However, the author is at present engaged in attempting to solve the radial wave equation for a Wentzel potential by means of converting it and its boundary conditions into an integral equation and solving by iteration. To date, it has been possible to extract the following facts. For particles of zero angular momentum, an integral equation equivalent to the radial wave equation and its boundary conditions is

$$w_0(r) = \sin(kr + \delta_0) + k^{-1} \int_r^\infty U(\xi) w_0(\xi) \sin k(\xi - r) d\xi. \quad (9)$$

The highest order approximation to the eigenfunction thus far found is the second; the eigenfunction is, to this

⁸ J. McDougall, Proc. Roy. Soc. (London) **A136**, 549 (1932).

order,

$$w_0(r) = \sin(kr + \delta_0) + (\lambda/4k) [-2 \cos(kr + \delta_0) E_1(\alpha r) + f(\mu, r) + f(\mu^*, r)] + (\lambda^2/8k^2) \{ \exp[-i(kr - \delta_0)] [g(\alpha, \mu, r) - g(\mu, \alpha, r)] + \exp[-i(kr + \delta_0)] [g(\mu, \mu^*, r) - \frac{1}{2}(E_1(\alpha r))^2] + \exp[+i(kr - \delta_0)] [g(\mu^*, \alpha, r) - g(\alpha, \mu^*, r)] + \exp[+i(kr + \delta_0)] [-g(\mu^*, \mu, r) + \frac{1}{2}(E_1(\alpha r))^2] \}. \quad (10)$$

The notation is as follows. $E_1(x) = \int_x^\infty (e^{-t}/t) dt$, the exponential integral; $f(\mu, r) = \frac{1}{2} \exp[-i(kr - \delta_0)] E_1(\mu r)$; $f(\mu^*, r) = \frac{1}{2} \exp[+i(kr - \delta_0)] E_1(\mu^* r)$, with α the quantity appearing in the Wentzel potential exponent, $\mu = \alpha - 2ik$, and $\mu^* = \alpha + 2ik$. A typical quantity g is given by

$$g(\gamma, \beta, r) = i \left\{ -E_1(\gamma r) - E_1(\gamma r) \ln \beta r - E_1^{(2)}(\gamma r) + \sum_n \frac{(-1)^{n-1}}{n \ln} \Gamma(\gamma r, n) \left(\frac{\beta}{\gamma} \right)^n \right\}.$$

In this expression $E_1^{(2)}(\gamma r) = \int_{\gamma r}^\infty (E_1(t)/t) dt$, and is tabulated by Kourganoff.⁹ The function $\Gamma(\gamma r, n)$ is the usual incomplete Γ function.

On application of the boundary condition $w_0(0) = 0$ to Eq. (10), one is led to a fairly simple expression for the phase shift. Unfortunately, this expression is little better than the Born approximation. For that reason, it will be discussed no further. However, inspection of (10) reveals a symmetry that promises hope that further iterations can be quickly made if only one term can be reduced to known integrals. It is hoped that a more complete account of the latter part of this discussion will be ready shortly.

The potentials developed in this paper have been applied to a consideration of finding atomic form factors, to a discussion of multiple scattering, and to the question of corrections for inelastic scattering and scattering in solids. These are discussed in the author's thesis¹⁰ and will not be covered here.

The author wishes to extend his thanks to Dr. Arthur E. Ruark for pointing out the usefulness of the potentials shown and for many discussions.

⁹ V. Kourganoff, *Basic Methods in Transfer Problems* (Clarendon Press, Oxford, 1952).

¹⁰ W. J. Byatt, thesis, University of Alabama, 1955 (unpublished).