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Critical Assessment of the Polarized-Orbital Method in Atomic Scattering

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Critical Assessment of the Polarized-Orbital Method in Atomic Scattering*

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The method of polarized orbitals used in calculating electron-atom scattering amplitudes has two obvious flaws: the wave function is discontinuous, and the method is not variationally based. These are corrected in a somewhat arbitrary manner, and it is found that the results then depend upon a parameter of the theory sufficiently strongly that there are serious doubts about the predictive nature of the theory.

I. INTRODUCTION

Techniques for calculating the scattering amplitude of an electron by an atom may be divided into three categories, predictive, checkable, or phenomenological. By the first we mean a no-parameter theory which purports to describe the situation. For example, the "optical potential" method was such an attempt.¹ It contains the static-exchange approximation with the variational inclusion of the long-range polarization effects. A prescription for the continuation of the polarization potential to small r was given with the expectation that the Pauli principle would make the results less dependent on the details of the cutoff. This expectation was borne out but not sufficiently to give quantitative agreement. That is, the cutoff parameter for the polarization potential still had to be chosen to give a fit with experiments. This then made the theory of the third type, the phenomenological. The close coupling method,² and its offshoots,³ are examples of our second category, the checkable ones, as are other variationally based calculations.⁴ By this we mean that when a basis is chosen for a variational calculation, the reliability of the results can usually be assessed by a comparison with an expanded basis.⁵

Theories of the first kind are the most ambitious and the most valuable. The method of polarized orbitals⁶ (p.o.) has been interpreted as such a theory and is becoming more widely relied upon as such.⁷ It is the object of this note to investigate the reliability of this method by correcting its obvious flaws and assessing its accuracy. In order to do this, we have presented (in the next section) a new ansatz for the trial form of the wave function. We emphasize here that this is not presented as a new and desirable way to calculate electron scattering but merely as a generalization of the p.o. method designed to assess its accuracy. Also in the next section, we discuss the simple case of s -wave electron-hydrogen singlet scattering. The singlet is chosen in that it is a more stringent test of the theory than is the triplet.

II. FORMAL DEVELOPMENT AND RESULTS

The p.o. method is designed to give an approximate solution for the scattering described by the Schrodinger equation

$$(E - H)\psi = 0 \quad (1)$$

The method is based on an assumed form for a scattering wave function, which for singlet s -wave

electron-hydrogen scattering is^{6,8}

$$\begin{aligned} \psi_{\text{p.o.}} = & A[u(r_1)/r_1][\varphi(r_2) \\ & - \epsilon(r_1 - r_2)(1/r_1^2)\chi_{S,p}(r_2, r_1)] \end{aligned} \quad (2)$$

where

$$A = 1 + X_{12} \quad (3)$$

and X_{12} exchanges coordinates 1 and 2. φ is the wave function of the ground state of hydrogen, and $\chi_{S,p}$ is the lowest-order distortion due to a distant stationary charge.

$$\chi_{S,p}(r_2, r_1) = \hat{r}_1 \cdot \hat{r}_2 (r_2 + \frac{1}{2}r_2^2)\varphi(r_2) \quad (4)$$

$\epsilon(r_1 - r_2)$ is a step function which is unity for $r_1 > r_2$ and vanishes otherwise. The scattering function $u(r_1)$ is determined by substituting (2) into (1) and then multiplying the result by $\varphi(r_2)$ and integrating over r_2 and the angular part of \hat{r}_1 . The choice of (2) is designed to include the polarization of the bound electron by the free one. It gives the long-range potential exactly and cuts it off by the prescription that there is no polarization when the incident electron is inside the bound one.

One disagreeable aspect of this method is the discontinuity (ϵ) built into the wave function. It is not admissible under the general rules of quantum mechanics. It causes no difficulty in the p.o. method because of the prescription for obtaining the equation for u . Another, but less powerful, objection is that the equation for u is not derived variationally and so could be improved.⁹ The use of the Kohn variational principle with the form (2) would result in infinities owing to the discontinuity in ϵ .

We have attempted to remedy both these defects by replacing the step function by a smooth one and then treating the problem variationally. The function, which we have chosen to replace ϵ , is an arbitrary function of the variable r_1/r_2 . This appears to us to be the simplest way of modifying (2) and still retain the content of the p.o. method. The new form of the trial function is now

$$\psi = A \frac{u(r_1)}{r_1} \left[\varphi(r_2) - \frac{f(r_1/r_2)}{r_1^2} \chi_{S,p}(r_2, r_1) \right], \quad (5)$$

where f is an arbitrary function. It could also be determined variationally, but the resulting equation is sufficiently complex so that it will not be treated numerically here. Clearly, (5) contains (2) as a special case, and if (2) is a good assumption,

then (5) is better.

The substitution of (5) into the form

$$I = \int d^3r_1 d^3r_2 \psi^*(E - H)\psi, \quad (6a)$$

and the variation with respect to $u(r)$, with the condition

$$\delta I = 0, \quad (6b)$$

results in⁸

$$\begin{aligned} [d^2/dr^2 + k^2 + Z(r)/r]v(r) \\ \pm \int_0^\infty dr' Q(r, r')v(r') = 0, \end{aligned} \quad (7)$$

where k^2 is the incident energy of the electron (in Rydbergs).

The new function $v(r)$ is related to $u(r)$ by

$$v(r) = [A(r)]^{1/2}u(r) \quad (8)$$

where

$$A(r) = \int_0^\infty dx x^2 \varphi^2(x) \left[1 + \frac{1}{3} \frac{x^2}{r^2} \left(1 + \frac{x}{2} \right)^2 f^2 \left(\frac{r}{x} \right) \right] \quad (9)$$

is essentially the normalization of the perturbed bound state. $A(r)$ is a constant for $r \rightarrow \infty$; so, the u and v yield the same phase shift. The boundary conditions are the usual ones for s -wave scattering, at $r=0$ and ∞ . The potentials in (7) are given by

$$Z(r) = r[A'^2/4A^2 + \Delta(r)/A] \quad (10)$$

$$\begin{aligned} \text{where } \Delta(r) = \int_0^\infty dx x^2 \varphi^2(x) [a_1 + a_2 f(r/x) \\ + a_3 f^2(r/x) + a_4 f'^2(r/x)] \end{aligned} \quad (11)$$

$$\text{and } a_1 = 2/r - 2h_0(r, x) \quad (12a)$$

$$a_2 = (4x/3r^2)(1 + x/2)h_1(r, x) \quad (12b)$$

$$\begin{aligned} a_3 = (x^2/3r^4)(1 + x/2)^2 [2/r - 2h_0(r, x) \\ - \frac{4}{5}h_2(r, x)] - \frac{2}{3}(x^2/r^4)(1 + x/2) \\ \times (1 - 2/r^2 + x^2/r^2) \end{aligned} \quad (12c)$$

$$a_4 = -(1/3r^4)(1 + x/2)^2(1 + r^2/x^2) \quad (12d)$$

where

$$h_l(r, x) = (1/r_{>})(r_{<}/r_{>})^l \quad (12e)$$

where $r_{>}(r_{<})$ is the greater (lesser) of x and r . The nonlocal potential is

$$Q(r, r') = A^{-1/2}(r)Q(r, r')A^{-1/2}(r'), \quad (13)$$

where

$$\begin{aligned} \bar{Q}(r, r') = & rr' \varphi(r) \varphi(r') \left\{ k^2 + 1 - 2h_0 + \frac{2}{3}h_1 \left[\frac{r'}{r^2} \left(1 + \frac{r'}{2} \right) f + \frac{r}{r'^2} \left(1 + \frac{r}{2} \right) \bar{f} \right] \right. \\ & + f \bar{f} \left[-\frac{2}{3rr'} \left(1 + \frac{r}{2} \right) \left(1 + \frac{r'}{2} \right) (h_0 + \frac{2}{5}h_2) + (k^2 - 1) \frac{1}{3rr'} \left(1 + \frac{r}{2} \right) \left(1 + \frac{r'}{2} \right) + \frac{1}{3rr'} \left(\frac{rr'}{2} - 2 \right) \right] \\ & + \bar{f} \bar{f}' \frac{2}{3r'^4} \left(\frac{r'^2}{2} - 1 \right) \left(1 + \frac{r}{2} \right) + f \bar{f}' \frac{2}{3r^4} \left(\frac{r^2}{2} - 1 \right) \left(1 + \frac{r'}{2} \right) + \bar{f} \bar{f}'' \frac{r}{3r'^5} \left(1 + \frac{r}{2} \right) \left(1 + \frac{r'}{2} \right) \\ & \left. + f \bar{f}'' \frac{r'}{3r^5} \left(1 + \frac{r'}{2} \right) \left(1 + \frac{r}{2} \right) \right\}, \end{aligned} \quad (14)$$

where the notation is $f = f(r/r')$ and $\bar{f} = f(r'/r)$, and a prime on f indicates a derivative with respect to the argument of the function.

Variation of (6) with respect to f , with the condition (6b), results in an equation for f of the form⁸

$$\begin{aligned} B_1 f''(x) + B_2 f'(x) + B_3 f(x) + B_4 \\ + \left[\Gamma_1 f'' \left(\frac{1}{x} \right) + \Gamma_2 f' \left(\frac{1}{x} \right) + \Gamma_3 f \left(\frac{1}{x} \right) + \Gamma_4 \right] = 0, \end{aligned} \quad (15)$$

where again the primes on f indicate derivatives with respect to the argument. The functions B_i and Γ_i are complicated functions of x which depend bilinearly on v . Equations (7) and (15) therefore constitute a nonlinear set of equations.

Equation (15) is an unusual form, a functional differential equation. However, it can be converted to a pair of coupled second-order differential equations with the introduction of a new function $g(x) = f(1/x)$. The optimum procedure now would be a solution of the coupled set (7) and (15) with the definition (8). This is a major computational task, which is not necessary for our purposes. Instead, we have solved (7) with various "reasonable" choices of f . The boundary conditions on $f(x)$ are

$$\lim_{x \rightarrow \infty} f(x) \rightarrow 1 \quad (16a)$$

$$\lim_{x \rightarrow 0} x^{-2} f(x) < \infty \quad (16b)$$

The first of these insures that (5) has the correct form when the scattered electron is well separated from the atom; the second is the condition that (5) be finite at $r_1 = 0$. An analysis of (15) shows that $f(x)$ behaves as x^3 for small x and differs from unity by terms of order $(x \ln x)^{-1}$ at large x .

Equation (7) describes the scattering of the electron in the local potential Z/r and the nonlocal one Q . We have investigated the behavior of the local potential in the limits $r \rightarrow 0$ and $r \rightarrow \infty$. For small r the effective charge $Z(r)$ becomes

$$Z(0) = 2C, \quad (17a)$$

where

$$C = 1 + \frac{2}{3} \int_0^\infty \frac{dx}{x^4} \left[\frac{4}{x^2} f^2(x) - (1+x^2) f'^2(x) \right]. \quad (17b)$$

Care must be taken in interpreting this as the effective charge at the origin. We are dealing with a nonlocal equation and the nonlocal part may also contribute a potential behaving as r^{-1} at the origin. In order to illustrate this and our method of numerical computation, we shall formally convert (7) into a local equation by the "Gammelizing" process.¹⁰ Equation (7) can be rewritten as

$$\left(\frac{d^2}{dr^2} + N \frac{d}{dr} + k^2 + \frac{Z}{r} + M \right) v = 0, \quad (18a)$$

where

$$M = \frac{1}{D(r)} \int_0^\infty dr' Q(r, r') v(r') v(r), \quad (18b)$$

$$N = \frac{1}{D(r)} \int_0^\infty dr' Q(r, r') v(r') v'(r) / k^2, \quad (18c)$$

$$D(r) = v^2(r) + v'^2(r) / k^2. \quad (18d)$$

The transformation

$$v(r) = \left[\exp\left(-\frac{1}{2} \int_0^r dr' N(r')\right) \right] w(r) \quad (19)$$

results in

$$\left(\frac{d^2}{dr^2} + k^2 + \frac{Z}{r} + M - \frac{1}{2} N' - \frac{1}{4} N^2 \right) w = 0. \quad (20)$$

This may now be interpreted as a scattering equation with a potential depending upon the scattering function through M and N . We must now investigate the behavior of these functions for small r in

order to determine the effective local potential at the origin. Simple but lengthy analysis yields the result that the integral

$$\int_0^\infty dr' Q(r, r') v(r')$$

behaves as r^0 for $r \rightarrow 0$. Hence the dominant potential term is indeed Z/r for $r \rightarrow 0$, and we obtain the result that the optimum potential with the form (5) has a fictitious charge at the origin of magnitude given by the second term in (17b). This result is purely a result of the form of the trial function; however, it does illustrate that statements concerning the way that the polarization potential should be cut off are not very meaningful. For instance, in contrasting the Buckingham form¹ ($-\alpha/(r^2+d^2)^2$) with the form obtained from the p.o. method, the latter has been given preference on the grounds that it vanishes at $r=0$ where the former does not. We believe that our result, while not particularly meaningful physically, has a better foundation than either of the above methods, and yet it introduces a singular potential at the origin of the form $2(C-1)/r$.

For large r , the nonlocal potential contribution vanishes exponentially and so may be dropped. We find that the dominant term is just the correct polarization (r^{-4}) potential as in the p.o. method. However, our next term in the potential is $-\frac{1229}{4} r^{-6}$, which is exactly the leading nonadiabatic contribution to the potential.¹¹ This contribution comes solely from the f^2 term in (11), and is independent of the details of f , depending only on the condition $f(\infty) = 1$. Bilinear terms in f in the potential can not arise in the p.o. method, and so this potential term can not arise there. There are of course additional r^{-6} contributions from the quadrupole polarizability in the actual potential. By adjusting f we can introduce additional r^{-6} terms in our potential, but they are repulsive whereas the quadrupole polarizability is attractive. We do not believe that this is a serious objection to this method or to the p.o. method in that the r^{-6} terms are dominated by the r^{-4} terms, which are correctly given, and moreover, both long range potentials are only important in the vicinity of thresholds.

Our numerical procedure for solving (7) was to first convert it to the form (18a) and then iterate by the following procedure: The potentials, M and N , are evaluated with some guess for v ; Eq. (18a) is then solved by standard means and the resulting v used for an improved evaluation of M and N . Convergence was obtained when the ratios of two successive phase shifts agreed to $\leq 10^{-4}$. Integration of (18a) was extended only out to $r = 10$. The remaining long-range potential was treated by first-order perturbation theory. We estimate that our numerical results are good to the figures quoted.

We have used the functional form

$$f(x) = x^n / (d^n + x^n) \quad (21)$$

with n and d as adjustable parameters. Roughly, d controls the region in which the jump in f takes place and n the steepness of the jump. The p.o. method is obtained from $d = 1$ and $n \rightarrow \infty$, but the potentials Z and Q become singular because of the

TABLE I. Phase shifts, in radians, for singlet s -wave scattering δ_0^+ for various values of n and d used to parametrize $f(x)$.

k	n d	7 1.0	5 2.0	5 1.0	3 1.0	3 0.8	3 1.2	3 1.4	3 1.6	3 1.8	3 2.0	3 3.0
0.1		2.300	2.415	2.295	2.273	2.017	2.390	2.444	2.467	2.474	2.473	2.444
0.2		1.745	1.889	1.740	1.718	1.494	1.848	1.917	1.948	1.959	1.959	1.926
0.3		1.368	1.522	1.364	1.345	1.158	1.466	1.536	1.571	1.584	1.586	1.558
0.4		1.079	1.246	1.076	1.061	0.895	1.176	1.246	1.283	1.299	1.303	1.281
0.5		0.843	1.030	0.842	0.829	0.673	0.942	1.015	1.056	1.076	1.082	1.066
0.6		0.649	0.861	0.647	0.636	0.482	0.752	0.831	0.877	0.901	0.909	0.901
0.7		0.485	0.731	0.485	0.475	0.320	0.598	0.684	0.737	0.764	0.777	0.772
0.8		0.349	0.635	0.350	0.341	0.181	0.470	0.567	0.628	0.662	0.678	0.678
0.9		0.235	0.562	0.237	0.229	0.062	0.370	0.476	0.545	0.584	0.603	0.611
1.0		0.139	0.512	0.142	0.134	-0.041	0.288	0.405	0.482	0.527	0.551	0.565

f'^2 term in (11) and the last two terms of (14). In Table I, results for various values of the param-

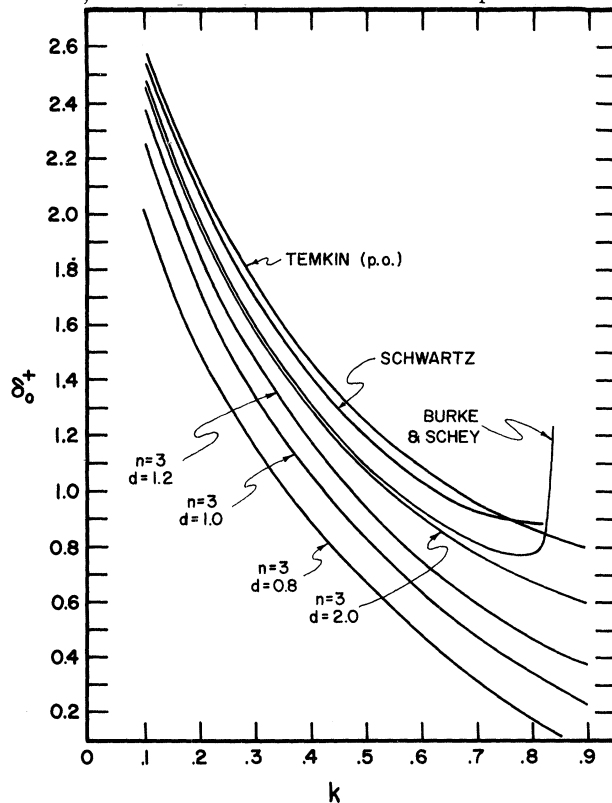


FIG. 1. Singlet s -wave phase shifts for some of our results and some results of previous calculations.

eters are presented along with results of other calculations. It is seen that for $d=1$, variation of n in the range 3, 5, 7 does not produce significant changes in the phase shift. Thus, the steepness of the transition of f is apparently not critical. However, variation of d does give significant differences as seen from the table and from the figure. This method gives a lower bound⁵ to the phase, as do the close coupling calculations of Burke and Schey¹² and the variational calculation of Schwartz,⁴ so that the larger the phase shift among these calculations the better the result. Referring to Fig. 1 and the Table, we see that larger values of d give better results, and for $d=2$ or 3, our results are essentially those of the three-state calculation of Burke and Schey¹² for most of the energy range. Actually, the $d=3$ results lie somewhat below the $d=2$ ones for most of the energy range so that we expect that we roughly have found the optimum f within the functional form of Eq. (21). It is clear that a solution of (15) and (7) would yield better phase shifts than the ones which we have found, but since this is not the object of this paper, we shall not pursue it here. The preference which we find for larger cut-offs may be interpreted as an indication that adiabatic criteria, which are used to motivate (2) and (5), should not be extended too close to the atom. This indication has appeared before.¹¹

In conclusion, we feel that the success of the p.o. method in giving phase shifts is not fully understood and that the apparently improved method presented here has enough dependence upon the arbitrary parameters inherent in the theory to eliminate it and the original p.o. method from the predictive class at this stage of our knowledge.

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Coupled-States Method for Scattering Calculations

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The eigenfunction-expansion method for calculating scattering of electrons and positrons from atoms has the very desirable property of providing phase-shift bounds, but is slowly convergent in some cases. Phase-shift bounds and improved convergence are combined in recently developed hybrid methods, but these are complicated to apply. An alternative method based on expansion in target states, some of which are chosen for best convergence rather than restricted to eigenstates, is proposed. The coupled equations are similar to those of the eigenfunction-expansion method and provide phase-shift bounds. The method was tested by calculation of S-wave positron-hydrogen scattering at energies of $k^2=0, 0.04, 0.16$, and 0.36 . Target states used in the expansions ($1s2p'$ and $1s2p'3d'$) were of the same functional form as eigenstates, except that orbital exponents were not fixed at $\frac{1}{2}$ and $\frac{1}{3}$. Calculated phase shifts as a function of orbital exponent value have a broad maximum for exponent values larger than those of eigenfunctions, and phase shifts are considerably larger than those calculated with eigenfunction expansions.

INTRODUCTION AND DISCUSSION

In calculating approximate solutions of the non-relativistic Schrödinger equation for atomic systems, it is desirable to have methods which are convenient to apply, converge rapidly, and lead to improved estimates of the relevant physical parameter as the approximation is increased in scope. A discussion is given of these properties as they apply to various methods of treating the scattering of positrons and electrons by atoms, as well as to bound-state calculations. A coupled-states scattering method, which is a modification of the familiar eigenfunction-expansion method, is proposed, and its effectiveness tested by application to S-wave scattering of positrons from hydrogen atoms.

Development of appropriate methods for treating scattering problems¹ has been more difficult than for bound states. Trial functions automatically provide an upper bound to the energy of the lowest discrete state of the same symmetry as the trial function²; hence variational estimates of energy necessarily improve as a trial function is made more flexible. Upper energy bounds are also provided for higher states by Rayleigh-Ritz calculations, involving variation of expansion coefficients, and sometimes by methods involving continuous variation of functions.³ Of intuitive appeal are expansions formed from products of eigenfunctions of a one-electron Hamiltonian. It has long been realized, however, that such expansions converge very slowly.⁴ This can be ex-

plained by noting that there are non-negligible contributions from continuum one-electron eigenstates. Alternatively, one can merely observe that the excited one-electron eigenfunctions become spatially quite diffuse, whereas extra flexibility of the trial function is needed in the vicinity of the nucleus. Thus, in spite of the elegance of eigenfunction expansions, it has proven desirable in bound-state problems to simply choose expansion states for best convergence.⁴

Similarly, it has been appealing to treat the scattering of positrons and electrons by atoms by the use of a trial function, expressed as a sum of products of target eigenstates with initially undetermined functions of coordinates of the scattered particle.⁵ The equations are separated by multiplying by each of the target states in turn, and integrating over target coordinates. The resulting set of differential or integrodifferential equations are then solved numerically. This eigenfunction-expansion method, often called the close-coupling method, is relatively straightforward in application. It has been extensively employed and has led to quite important results, including prediction of scattering resonances,⁶ but the convergence properties have turned out to be rather poor in some cases.⁵

By analogy with bound-state problems, one might expect improvement in convergence, if the expansion states were chosen to be spatially compact rather than restricting them from the outset to target eigenstates. This possibility has been mentioned by various authors,^{5,7} but has not been