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Electron–Alkali-Atom Scattering—A Nonadiabatic Approach*

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The nonadiabatic method of Temkin which has been applied to electron-hydrogen scattering is generalized to the problem of electron-alkali scattering. A two-body equation is derived in which the core of the atom has the principal effect of modifying the two-body interaction and of excluding the two extra-core electrons from the occupied states of the core. This equation may be viewed as a generalization of the Bethe-Goldstone equation for the problem of scattering from a finite system.

I. INTRODUCTION

MOST methods for the calculation of the scattering of low-energy electrons by atoms are based upon a method for reducing the many-body problem to a one-body problem in the presence of an external potential. This results in the one-body Schrödinger equation, an integro-differential equation or set of coupled integro-differential equations, which is usually solved numerically. *All* these methods may be viewed as approximation schemes in the equivalent-potential method.[1] This method breaks the Hilbert space into two pieces. The first is relevant to the scattering problem, while the second is orthogonal to it and presumably only loosely coupled to it. An exact equation is derived for the part of the total wave function spanned by the first part of the Hilbert space. The second part enters this equation only through a potential in the equation. This equivalent potential is a result of virtual transition in and out of the second part. It is always difficult to approximate, and *all* the methods mentioned above can be viewed as ways of approximating the equivalent potential. For instance, the close-coupling method[2] simply discards the higher terms in the equivalent potential, even though their long-range behavior, which can be obtained exactly, actually dominates the long-range behavior of the terms retained.[3] A modification of the close-coupling method[3] which includes these long-range effects suffers from the ambiguity in the cutoff of these effects. That is, when long-range terms of the potential behaving like r^{-4}, for instance, are kept they must be cut off at short range. The equivalent potential contains this cutoff but it is difficult to calculate, so in practice a phenomenological cutoff function has to be introduced. The method of polarized orbitals[4] is one technique for introducing such a cutoff. It and most others rely on an adiabatic approximation for the calculation of the cutoff. It is based on the assumption that the incoming electron moves slowly compared to the bound ones so that the atom may deform adiabatically as a result of the interaction with the projectile. When the projectile is far enough away the approximation is a good one, but as it approaches the atom the approximation breaks down. Indeed, it would seem to break down more rapidly for more polarizable atoms.

The Pauli principle was thought to be the saving feature of the problem. A consistent derivation of the equivalent potential with account of the antisymmetry of the wave function under interchange of the projectile and target particles *requires* among other things that the scattered wave function be orthogonal to the occupied orbitals of the atom (a Hartree-Fock description of the atom is implied here, although a generalization to more complicated wave functions has been given).[1] For heavy atoms and slow electrons this requirement tends to exclude the electron from the interior of the atom. This reduces the dependence of the phase shift upon the ambiguities of the short-range behavior of the equivalent potential. This expectation has been confirmed by explicit numerical calculation.[5] Unfortunately, this qualitative effect does not appear to be enough to allow a completely predictive theory of electron-atom scattering.

The success of the close-coupling method in electron-hydrogen scattering indicates that the long-range terms which are dropped are not important in the actual problem. It is known that these r^{-4} terms are important in the vicinity of zero energy and near thresholds but it seems that they are cutoff in such a way as to give a negligible contribution to the scattering at intermediate energies. Calculations with different but reasonable "cutoff functions" in the equivalent potential yield significantly different phase shifts and there does not appear to be any *a priori* method for justifying one over the other.

The method of polarized orbitals has also been successful in giving reasonably good results for various atoms. It can be presented as a variationally based calculation. The trial wave function is taken as a fully antisymmetrized product of an unknown scattering function of the scattering coordinate and a modified atomic wave function. The modification depends upon the scattering coordinate and allows for the adiabatic deformation of the ground state by the scattered

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particle. This introduces the ambiguity of a cutoff function into the wave function instead of into the equivalent potential. The equation of motion for the scattering function will contain an approximation to the equivalent potential which will reflect this ambiguity. Again the hope is that the symmetry of the total wave function will minimize the effect of this ambiguity but this has not been demonstrated in that only one form of the cutoff function has been used. In any case, no matter how the derivation is presented it may be shown that the error in the tangent of the phase shift is proportional to the error in the equivalent potential.

Temkin's nonadiabatic method[6] does not fit directly into the above outline. It has been applied only to hydrogen where it deals directly with the equation of the two electrons in the Coulomb potential of the nucleus. The approximation procedure is one of expanding the wave function in a relative partial-wave series. We illustrate for total angular momentum equal to zero. The total wave function Ψ can be considered a function of the three variables r_1, r_2, μ, where r_1 and r_2 are the distances of the electrons from the nuclei and $\mu=\hat{r}_1\cdot\hat{r}_2$. The function is expanded as

$$\Psi=\sum_l \psi_l(r_1,r_2)P_l(\mu)\,,$$

and only a small ($l=0$, 1) number of terms are retained. The result is a system of coupled partial differential equations. The method accounts for the correlation of the two electrons more accurately than the methods described above. More of the long-range potential is included and no cutoff procedure is necessary. The method is equivalent to including all $l=0$ and 1 states in the close-coupling method.

It seems appropriate to raise the problem of the generalization of this method for heavier atoms, in particular for alkalis where the improvement will probably be greatest. This is accomplished in the next section.

II. FORMAL DERIVATION

The nonadiabatic method as applied by Temkin to electron-hydrogen scattering starts from the full equation for two bodies in an external field. For the problem of electron-alkali scattering we therefore seek an analogous two-body equation, but we may expect that all the interaction potentials will be more complicated. We shall make the usual assumption of neglecting spin-dependent forces so that the singlet and triplet scatterings decouple. Let the two-body wave functions describing these be $\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)$ with the symmetry

$$\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)=\pm\chi_\pm(\mathbf{r}_1,\mathbf{r}_0)\,. \tag{1}$$

The first problem we encounter is that of defining this function in terms of the full wave function $\Psi_\pm(\mathbf{r}_0,\mathbf{r}_1,\cdots,\mathbf{r}_z)$. That is, again we break the Hilbert space into two pieces. The first one, spanned by a projection operator $P_\pm$, which we want to determine, will contain the function $\chi_\pm$, while the other spanned by the projection operator $Q_\pm=1-P_\pm$ will be formally eliminated. The problem is how do we define $\chi_\pm$. One approach is to write

$$\begin{aligned} P_\pm\Psi_\pm&=A\chi_\pm(\mathbf{r}_0\mathbf{r}_1)(1/\sqrt{2})\\ &\qquad\times[\phi_+(1\cdots z)\sigma_-(0)\mp\phi_-(1\cdots z)\sigma_+(0)]\\ &=A\chi_\pm\Delta_\pm\,, \end{aligned} \tag{2}$$

where $\phi_\pm$ is the ground-state wave function of the alkali (spin and space), and the subscript denotes the spin direction. $\sigma_\pm(0)$ is the spin wave function of particle "0." The wave functions $\phi_\pm$ are antisymmetric in their arguments and A is the appropriate antisymmetrization operator. The equation for $P_\pm$ arises from the requirement that all the scattering be contained in $P\Psi$.

$$S_0\int d_2\cdots d_z\Delta_\pm^*(1-P_\pm)\Psi_\pm=0\,. \tag{3}$$

Here[7] we use the notation that S_i is the spin sum on coordinate i and $d_i=S_i d^3r_i$. This leads to an intractable equation for P, even when one makes a Hartree-Fock approximation for ϕ. In addition, it is difficult to obtain the symmetry (1) with this definition. We therefore try a less ambitious definition which will lead to restrictions on the method. We replace (2) by the equation

$$\begin{aligned} P_\pm\Psi_\pm&=A\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)\psi(2\cdots z)\\ &\qquad\times(1/\sqrt{2})[\sigma_-(0)\sigma_+(1)\mp\sigma_+(0)\sigma_-(1)]\\ &=A\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)D_\pm(01,2\cdots z)\,, \end{aligned} \tag{4}$$

where $\psi(2\cdots z)$ is the normalized and antisymmetrized ground-state wave function of the alkali ion. The asymptotic form of the total function $\Psi_\pm$ is

$$\begin{aligned} \lim_{r_0\to\infty}\Psi_\pm&\to\left(e^{i\mathbf{p}\cdot\mathbf{r}_0}+f_\pm\frac{e^{ipr_0}}{r}\right)\\ &\qquad\times\frac{1}{\sqrt{2}}[\phi_+(1\cdots z)\sigma_-(0)\mp\phi_-(1\cdots z)\sigma_+(0)]\,, \end{aligned} \tag{5}$$

where, for simplicity, we have taken only the elastic channel. We would like the asymptotic form of (4) to coincide with (5). To that end we can have

$$\lim_{r_0\to\infty}\chi_\pm\to\left(e^{i\mathbf{p}\cdot\mathbf{r}_0}+f_\pm\frac{e^{ipr_0}}{r_0}\right)\xi(r_1)\,. \tag{6}$$

If we now demand that

$$\lim_{r_0\to\infty} r_0(1-P_\pm)\Psi_\pm=0 \tag{7}$$

which is the statement that the Q part of Hilbert space

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[6] A. Temkin, Phys. Rev. **126**, 130 (1962).

[7] Actually this equation could be written only in its asymptotic form $r_0\to\infty$, but we use the stronger statement (3) here.

have no scattered wave, we obtain

$$\lim_{r_0\to\infty} r_0\left(e^{i\mathbf{p}\cdot\mathbf{r}_0}+\frac{e^{ipr_0}}{r_0}f_\pm\right)\frac{1}{\sqrt{2}}\{\sigma_-(0)[\phi_+(1\cdots z)-\hat{A}(\xi(r_1)\sigma_+(1)\psi(2\cdots z))]$$
$$\mp\sigma_+(0)[\phi_-(1\cdots z)-\hat{A}(\xi(r_1)\sigma_-(1)\psi(2\cdots z))]\}=0,$$

where $\hat{A}$ is the operator which antisymmetrizes the object upon which it acts. This requires that the coefficients of $\sigma_\pm(0)$ individually vanish.

$$\phi_\pm(1\cdots z)=\hat{A}[\xi(r_1)\sigma_\pm(1)\psi(2\cdots z)]. \tag{8}$$

This says that the atom is composed of a core plus an additional electron and that the core is identical to the ion. That is, that the valence electron does not perturb the core. This is a good approximation for the heavy alkalis, but not for lithium. We shall adopt this approximation for the rest of this paper and in addition describe the core by a Hartree-Fock wave function

$$\psi(2\cdots z)=[(z-1)!]^{-1/2}\det|\gamma_{j\pm}(i)|,\quad i=2\cdots z, \tag{9}$$

where the orbitals are given

$$\gamma_{j\pm}(i)=g_j(\mathbf{r}_i)\sigma_\pm(i),\quad j=1\cdots\tfrac{1}{2}(z-1). \tag{10}$$

With these approximations we now define $P_\pm$ by the requirement that there be no component of $Q_\pm\Psi_\pm$ which lies in the subspace with the core in its ground state.

$$S_{01}\int D_\pm{}^*(01,2\cdots z)(1-P_\pm)\Psi_\pm d_2\cdots d_z=0. \tag{11}$$

We define

$$\hat{\chi}_\pm(\mathbf{r}_0,\mathbf{r}_1)=S_{01}\int d_2\cdots d_z D_\pm{}^*(01,2\cdots z)\Psi_\pm, \tag{12}$$

and use Eq. (4) with

$$A=1-\sum_{j=2}^{z}(X_{ij}+X_{0j})+\tfrac{1}{2}\sum_{j\neq k=3}^{z}X_{1j}X_{0k}, \tag{13}$$

where X_{jk} exchanges the coordinates j and k (spin and space). Some straightforward manipulations of (11) yield

$$\hat{\chi}_\pm(\mathbf{r}_0,\mathbf{r}_1)=\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)-\int K_\pm(\mathbf{r}_0\mathbf{r}_1,\mathbf{r}_0{}'\mathbf{r}_1{}')\chi_\pm(\mathbf{r}_0{}',\mathbf{r}_1{}')d^3r_0d^3r_1, \tag{14}$$

where

$$K_\pm(\mathbf{r}_0\mathbf{r}_1,\mathbf{r}_0{}'\mathbf{r}_1{}')=\delta(\mathbf{r}_0-\mathbf{r}_0{}')\sum_j g_j(\mathbf{r}_1)g_j{}^*(\mathbf{r}_1{}')+\delta(\mathbf{r}_1-\mathbf{r}_1{}')\sum_j g_j(\mathbf{r}_0)g_j{}^*(\mathbf{r}_0{}')$$
$$-\tfrac{1}{4}\sum_{jk}[g_j(\mathbf{r}_0)g_k(\mathbf{r}_1)\pm g_j(\mathbf{r}_1)g_k(\mathbf{r}_0)][g_j(\mathbf{r}_0{}')g_k(\mathbf{r}_1{}')\pm g_j(\mathbf{r}_1{}')g_k(\mathbf{r}_0{}')]^*. \tag{15}$$

The sums here and below run over the $\frac{1}{2}(z-1)$ different occupied orbitals. Equation (14) is an integral equation for $\chi_\pm$. Following Feshbach[1] it is solved in terms of the eigenfunctions of $K_\pm$ defined by

$$\lambda K_\pm U_\lambda(\pm)=U_\lambda(\pm),\quad \langle U_\lambda(\pm)U_\lambda(\pm)\rangle=\delta_{\lambda\lambda'}. \tag{16}$$

In terms of these we get

$$\chi_\pm=\left[1+\sum_{\lambda\neq1}\frac{U_\lambda(\pm))\langle U_\lambda(\pm)}{\lambda-1}\right]\hat{\chi}_\pm \tag{17}$$

and we also obtain

$$\langle U_{\lambda=1}(\pm)\chi_\pm\rangle=0, \tag{18}$$

which is the orthogonality requirement resulting from the Pauli principle. The kernel, (15), is degenerate and all its eigenvalues are unity. The eigenfunctions are the appropriately symmetrized combinations of the product $g_a(\mathbf{r}_0)g_b(\mathbf{r}_1)$, where at least one of g_a and g_b is an orbital occupied in ψ. Using the completeness of *all* the functions g_j, Eq. (18) may be written

$$\int d^3r_0g_j{}^*(\mathbf{r}_0)\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)=\int d^3r_1g_j{}^*(\mathbf{r}_1)\chi_\pm(\mathbf{r}_0,\mathbf{r}_1)=0 \tag{19}$$

which is the physically reasonable statement that neither of the electrons in $\chi_\pm$ can get into a core state.

Combining (17), (11), and (12) we may infer that

$$P_\pm=(A/\sqrt{N})D_\pm\rangle\delta(\mathbf{r}_0-\mathbf{r}_0{}')$$
$$\times\delta(\mathbf{r}_1-\mathbf{r}_1{}')\langle D_\pm(A/\sqrt{N}), \tag{20}$$

where $N=\frac{1}{2}z(z+1)$.

The equation for $P_{\pm}\psi_{\pm}$ may be obtained directly from the Schrödinger equation which we write as

$$(E-H)P_{\pm}\Psi_{\pm}+(E-H)Q_{\pm}\Psi_{\pm}=0. \tag{21}$$

Multiplication from the left with $P_{\pm}$ and then with $Q_{\pm}$ yields a pair of coupled equations. If $Q_{\pm}\Psi_{\pm}$ is eliminated, the usual result is obtained

$$[E-P_{\pm}\mathcal{H}_{\pm}P_{\pm}]P_{\pm}\Psi_{\pm}=0, \tag{22}$$

where

$$\mathcal{H}_{\pm}=H+H[Q_{\pm}/(E-Q_{\pm}HQ_{\pm})]H. \tag{23}$$

Here E is the total energy and H is the Hamiltonian. The equation for $\chi_{\pm}$ is obtained by the operation $\langle D_{\pm}(01,2\cdots z)$ on Eq. (22). Using the result

$$\langle D_{\pm}AD_{\pm}\rangle=1-K_{\pm},$$

and

$$K_{\pm}\chi_{\pm}=0, \tag{24}$$

which follow directly from (19), the equation is

$$E\chi_{\pm}-(1-K_{\pm})\langle D_{\pm}\mathcal{H}AD_{\pm}\rangle\chi_{\pm}=0. \tag{25}$$

The orthogonality relation (19) follows immediately from the form of (25) because the operator

$$\int d^3r_1 g_a{}^*(\mathbf{r}_1)K_{\pm}(\mathbf{r}_0\mathbf{r}_1,\mathbf{r}_0'\mathbf{r}_1')-g_a{}^*(\mathbf{r}_1')\delta(\mathbf{r}_0-\mathbf{r}_0')$$

vanishes when operating on a function with the symmetry of $\chi_{\pm}$, [Eq. (1)]. Thus Eq. (25) has the same property as the one-particle equivalent-potential equations; the Pauli principle tends to exclude both electrons from the interior of the core.

If we make the approximation of neglecting core excitations, the Q which projects onto excited core states may be set equal to zero and $\mathcal{H}_{\pm}=H$. Equation (25) then may be written more explicitly as

$$(k^2+W_0-W_0{}^+)\chi_{\pm}+(1-K_{\pm})\times(\nabla_0{}^2+\nabla_1{}^2-V_{\mathrm{HF}}(0)-V_{\mathrm{HF}}(1)-2/r_{10})\chi_{\pm}=0. \tag{26}$$

Here V_{HF} is the Hartree-Fock potential of the core

$$V_{HF}(\mathbf{r}_0,\mathbf{r}_0')=\delta(\mathbf{r}_0-\mathbf{r}_0')\left(V(r_0)-\frac{2z}{r_0}\right)-2\sum_j\frac{g_j(\mathbf{r}_0)g_j{}^*(\mathbf{r}_0')}{|\mathbf{r}_0-\mathbf{r}_0'|}, \tag{27}$$

where

$$V(r)=2\int d^3x\frac{\rho(x)}{|\mathbf{x}-\mathbf{r}|},$$

and $\rho(x)$ is the electron density of the core. W_0 is the ground-state energy of the atom and $W_0{}^+$ that of the ion. $K_{\pm}$ is the integral operator (15). The kinetic-energy and Hartree-Fock operators are both one-particle operators. This fact, coupled with the orthogonality statement (19), results in a simplification of the form

$$K_{\pm}(-\nabla_1{}^2+V_{\mathrm{HF}}(1))\chi_{\pm}. \tag{28}$$

In this term $K_{\pm}$ immediately becomes

$$K_{\pm}\rightarrow\delta(\mathbf{r}_0-\mathbf{r}_0')\sum_j g_j(\mathbf{r}_1)g_j{}^*(\mathbf{r}_1').$$

Now, using the equation defining g_j, the form (28) becomes

$$\sum_j g_j(r_1)\epsilon_j\int d^3r_1'g_j{}^*(r_1')\chi_{\pm}(\mathbf{r}_0,\mathbf{r}_1')=0$$

so that (26) becomes

$$(k^2+\Delta_i)\chi_{\pm}(\mathbf{r}_0,\mathbf{r}_1)+[\nabla_0{}^2+\nabla_1{}^2-V_{\mathrm{HF}}(0)-V_{\mathrm{HF}}(1)-(1-K_{\pm})2/r_{10}]\chi_{\pm}=0. \tag{29}$$

Thus the presence of the core only modifies the two-electron interaction. A factor $(1-K_{\pm})$ could be inserted to the right of $2/r_{10}$ to make the interaction explicitly Hermitian. Here Δ_i is interpreted as the ionization potential of the atom. The boundary conditions are

$$\lim_{r_0\rightarrow\infty}\chi_{\pm}\rightarrow(e^{i\mathbf{p}\cdot\mathbf{r}_0}+f_{\pm}e^{ipr_0}/r_0)g(\mathbf{r}_1),$$

where $g(r)$ is the Hartree-Fock orbital of the valence electron of the atom which by the assumption of Eq. (8) is the same as the first unoccupied orbital in the potential (27). The symbol $f_{\pm}$ is the scattering amplitude.

Equation (29) is just the finite-system Bethe-Goldstone equation[8] for a scattering problem.

Note added in proof. The reasoning followed here required two assumptions. The first is Eq. (8) which identifies the "core" with the ion, the second, Eq. (9) makes a Hartree-Fock assumption for the core. The net is a Hartree-Fock assumption for the whole atom. If the Hartree-Fock assumption for the atom were made immediately there would be no need to introduce the ion and consequently the first assumption would be obviated. Thus the final equations should be as applicable to lithium as to the heavy atoms.

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[8] H. A. Bethe and J. Goldstone, Proc. Roy. Soc. (London) **A238**, 551 (1957).