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Application of the Pseudopotential Method to Atomic Scattering.

Panayiotis Sophocleous Laghos

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APPLICATION OF THE PSEUDOPOTENTIAL METHOD
TO ATOMIC SCATTERING

A Dissertation

Submitted to the Graduate Faculty of the
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in partial fulfillment of the
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in

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by
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ABSTRACT

The empirical pseudopotential method is discussed. Wave functions for the free sodium and cesium atoms which agree well with the exact valence electron functions at large distances are obtained by numerical solution of the wave equation incorporating the pseudopotential. A Heitler-London calculation is made for the lowest singlet and triplet states of the Na - Cs system. The difference in energies of these states is used in the calculation of the spin exchange cross section in collisions of sodium and cesium atoms. The scattering phase shifts are calculated in the JWKB approximation, and the cross section computed from them is averaged over a Boltzmann distribution of relative velocities. At a temperature of 500°K, the averaged reduced spin exchange cross section is $1.48 \times 10^{-14} \text{ cm}^2$.

The effect of elastic scattering on the cross section for electronic excitation in the collisions of slow atoms interacting by Van der Waals forces is estimated, and found to be small in usual circumstances.

I INTRODUCTION

Knowledge of interatomic potentials is of fundamental importance in many problems in physics, astronomy, and chemistry. In the case of atoms with few electrons reasonably accurate Quantum Mechanical calculations from first principles are possible. For heavier atoms, however, great mathematical and computational difficulties arise. In this respect, a class of atoms having only one valence electron and that in a s state, i.e. the alkalis, deserve special consideration. As a first step one can think of the alkalis as one-electron atoms with the single electron moving in a non-coulomb field. The second step is to realize that the effects of electrons in closed shells are not removed entirely (by the first step) because even in low energy problems where only the valence electrons are of real interest, it is still necessary to consider the orthogonality of the valence electron wave function to the wave functions of electrons in closed shells in both of the interacting atoms. Thus it is desirable to remove the core electrons from the problem completely. This is accomplished by the pseudopotential discussed in sec. IV.

When two alkali atoms in their ground states approach each other, two spin states are possible, a singlet and a triplet, and each of these has its own potential energy curve. In the present case we are interested in spin exchange scattering which, in the semi-classical approximation, depends on the difference between these two energy curves.

Moreover, we are interested in atomic interactions at moderately large separations where there is no overlap of the wave functions of core electrons, and we propose to calculate the difference in potentials in the Heitler-London approximation. (See Sec. V).

The Hamiltonian for a system of interacting Na and Cs atoms is set up, using the atomic pseudopotentials. The total wave function for the interacting system is approximated by a properly antisymmetrized product of functions of the individual electrons. For these separate functions one uses the wave functions resulting from solving the wave equation for each of the individual free atom (participating in the interaction) making use of the pseudopotential. Undoubtedly this is not exact. For an improved calculation one would have to consider also explicitly the excited states of the atoms. However, it certainly is a reasonable approximation for the lowest states of the quasi-molecule.

The spin exchange cross section, (Sec. VI), for the scattering of alkali metal atoms is determined by the difference in potential energy curves between singlet and triplet states, and since the atomic states involved are s states, this difference will be unaffected by a common Van der Waals potential. It is proper to note at this point that other atoms introduce not only the difficulty of having more electrons but of having them in p or d shells in which case the angular dependent part of the Van der Waals force would have to be taken into consideration.

A thesis on atomic interactions, however, cannot be complete until the effects of elastic scattering (deviations from straight

line trajectory) are examined. The excitation of an atom in a collision with another atom in a situation in which the dominant interaction is the Van der Waals interaction has been studied.^{1,2} It is, therefore, interesting to obtain a quantitative measure of the effect of elastic scattering on the cross section of electronic excitation in the collision of slow atoms interacting by Van der Waals forces.³ This is done in Sec. III .

II INTERATOMIC POTENTIALS - BRIEF LITERATURE REVIEW

The study of atomic interactions presents us with the difficulties of the many electron problem which we cannot handle exactly but can only treat by approximate methods. In the limit of two atoms approaching each other very slowly, the concept of an interatomic potential energy function, $V(R)$, has become very useful. It has been extensively used in the study of a considerable range of phenomena associated with the equation of state and transport properties of gases and solids. For example, classical statistical mechanics relates $V(R)$ to the temperature-dependent second virial coefficient, $B(T)$, through the equation⁴

$$B(T) = 2\pi N_0 \int_0^\infty \left[1 - \exp\left(-\frac{V(R)}{KT}\right) \right] R^2 dR \quad (2.1)$$

where N_0 is Avogadro's number, R is the interatomic separation and K is the Boltzmann constant, with quantum corrections, $\Delta B(T)$ given by

$$\Delta B(T) = \frac{h^2}{\mu} \frac{N_0}{24\pi K^3 T^3} \int_0^\infty \exp\left(-\frac{V(R)}{KT}\right) \left(\frac{dV(R)}{dR}\right)^2 R^2 dR \quad (2.2)$$

In (2.2) h is Planck's constant, μ is the reduced mass of the two atoms whose interaction is described by the potential $V(R)$. Also the kinetic theory of gases relates it to the transport properties of gases (coefficients of viscosity η , diffusion D , and heat conductivity λ) through the general integral^{4,5}

$$\Omega(\ell, r) = (2\pi KT/\mu)^{\frac{1}{2}} \int_0^\infty \int_0^\pi \exp(-\gamma^2) \gamma^{2r+3} (1 - \cos^\ell \theta) \times \\ I(\gamma, \theta) \sin \theta \, d\theta \, d\gamma \quad (2.3)$$

with

$$\gamma^2 = \frac{1}{2} \frac{\mu v^2}{KT} = \frac{E}{KT} \quad (2.4)$$

and $\ell = r = 1$ for D, and $\ell = r = 2$ for η and λ .

In (2.3) $V(R)$ enters the equation through the differential cross-section $I(\gamma, \theta)$.

Despite the usefulness of the interatomic potential we have not been able to develop a method simple enough for calculating it, especially at small interatomic separations where the forces are repulsive. For large separations, London⁶ has proved by quantum theory that the interaction potential should be proportional to $-R^{-6}$. The trend has therefore been to invent mathematical models which would be (i) adequate in the region of repulsive as well as attractive forces, (ii) applicable to a large number of systems and, (iii) simple enough to be used in calculations.

The various analytic expressions being used contain one, two or more arbitrary parameters which are determined by using these potentials to fit experimental data for gases (e.g. viscosities, virial coefficients), the crystalline state (e.g. equilibrium properties of the crystal like the entropy, energy, and density), etc. This procedure had great successes with systems that are chemically non-reacting (e.g. the inert gases) or having repulsive electronic states (e.g. the $^3\Sigma$ state of Na_2). It has not, however,

been uniformly successful. For example it is possible to obtain a set of parameters for some form of the potential which would fit experimental data for, say, the second virial coefficient for Argon in its gaseous state but the same set of parameters would give a poor fit to the experimental data for its viscosity.⁷ Furthermore, with chemical interactions a too simple form for the potential is no longer satisfactory because it cannot adequately describe the exchange attractions which depend strongly on the nature of the atoms involved.

In figures 1 and 2 we present some of the types of interatomic potentials used for systems having spherical symmetry. Applications, merits, and regions of applicability of each of these as well as many others have been presented by several authors^{4,7-12} and we will not dwell on them here any further.

At this point it is appropriate to give a word of caution. The whole concept of interatomic potential breaks down if the change in the energy of interaction within a distance of one De Broglie wavelength ($\lambda = h/\mu v$) is comparable to the separation between this and another potential energy curve¹³. Furthermore, in cases where two potential energy curves approach each other at some interatomic separation that is not too large, so that the interaction is still strong enough to cause transitions, then even slow collisions do not follow a single potential energy curve.

FIG. 1

FIG. 2a

FIG. 2 b

III ELASTIC SCATTERING AND INELASTIC TRANSITIONS

The studies considered by Callaway et.al.^{1,2} have employed the impact parameter method: the motion of the heavy particle was treated classically, and both the change in speed due to loss or gain of energy during the excitation, and the change in direction of motion due to elastic scattering were ignored.

Although cross sections computed using these methods are in reasonable agreement with experiment, we believe it is important to consider possible corrections to these approximations.³ Consider, for example, the reaction

The energy difference between the states is .002eV. This process has a cross section $\sigma \approx 0.6 \times 10^{-14} \text{ cm}^2$ at energies of about 400°K. If we consider a characteristic length for this reaction $\ell_0 = (\sigma/\pi)^{1/2}$, the strength of the Van der Waals potential at distance ℓ_0 is close to the initial kinetic energy. Therefore it is desirable to investigate elastic scattering by the Van der Waals potential.

The theory of the elastic scattering of atoms has been extensively studied by Ford and Wheeler¹⁴. We will confine our attention here to grazing collisions in which the short range repulsive forces between the atoms are unimportant.

Our approach is based on ref. 1, to which the reader is referred for the notation and for a more complete discussion of the methods

employed. The transition amplitude is found from an approximate solution of the time dependent Schrodinger equation. The interaction matrix elements are functions of R , the distance between the colliding atoms (and of angles also, which we neglect). We consider a scattering potential $V_s = -c/R^6$. We write $R(t) = (p^2 + v^2 t^2)^{1/2} (1 + f(t))$. A differential equation for f is readily obtained and solved under the restriction that only terms linear in c are included. The result is:

$$f(t) = -c \frac{1 + \frac{v^2 t^2}{p^2 + v^2 t^2} + \frac{3 vt}{2p \arctan vt/p}}{\mu v^2 p^6 (1 + v^2 t^2 / p^2)} \quad (3.1)$$

Here μ is the reduced mass of the colliding atoms, v the relative velocity, and p the impact parameter.

The inelastic processes will be described in a two level model. It is assumed that the transition is produced by Van der Waals interactions. We put $\langle 1 | V_s | 2 \rangle = q/R^6$, $\langle 1 | V_s | 1 \rangle = -\langle 2 | V_s | 2 \rangle = r q/R^6$. Thus r , here, measures the ratio of diagonal to off diagonal elements. Assume that the system was originally in state 1. The amplitude for it to be in state 2 at $t = \infty$ is found to be

$$|\alpha_2(p)|^2 = \eta^{-2} \left(1 - \frac{x^2 \eta^2}{3\eta^2} \sin^2 \left[\left(\frac{b}{p^5} + \frac{d}{p''} \right) \left(1 - \frac{x^2}{6\eta^2} \right) \right] \right) \quad (3.2)$$

where $\eta^2 = 1 + r^2$, $x = \omega p/v$, $b = 3\pi q \eta / 8 \mu v$, $d = 315 \pi q c \eta / 128 \mu v^3$.

Eq. (3.2) is exact for the model if $\omega = 0$.

The cross section is determined by

$$\sigma = 2\pi \int_0^{\infty} |\alpha_2(p)|^2 p \, dp$$

This integral cannot be done exactly even if $\omega = 0$. However, we are interested in terms linear in c . To estimate these, we approximate $\sin^2 \xi$ by $1/2$ when the argument is larger than a number k of order unity, and by $1/\xi^2$ when it is smaller than k . We choose for k the value 1.18 which yields agreement with the known exact value of σ , $\sigma(0)$ for $d = 0$ and $\omega = 0$. In the final expression for σ we retain the terms linear in c and ω^2 , plus the cross term between them. For simplicity we also set $r = 1$. The result is

$$\begin{aligned} \sigma = \sigma(0) \left[1 + 0.142 \frac{c}{|q|} \frac{\hbar}{\mu v \ell_0} - 0.463 \left(\frac{\omega \ell_0}{v} \right)^2 + \right. \\ \left. 0.588 \left(\frac{\omega \ell_0}{v} \right)^2 \frac{c}{|q|} \frac{\hbar}{\mu v \ell_0} \right] \end{aligned} \quad (3.3)$$

The significance of this expression is not the specific numbers but the general behaviour of the function. Elastic scattering increases the cross section. This is expected, since the attractive force pulls the colliding particles closer together and thus increases their interaction. Moreover, we find that the effect depends on the ratio of the wave length for a particle of mass equal to the reduced mass of the pair to the length ℓ_0 characterizing the cross section. This ratio is small for heavy particles except at very low speeds. For Na - Ar collisions, $\hbar/\mu v \ell_0 = 0.013$ at a speed corresponding

to 400°K (using $\sigma(0) = .66 \times 10^{-14} \text{cm}^2$) [1] , and even for the relatively unfavourable case of oxygen-hydrogen collisions studied in ref. 2, we have for $\sigma(0) = 4.2 \times 10^{-16} \text{cm}^2$ a speed corresponding to 400°K , $\hbar/\mu v \ell_0 = 0.22$. The term in eqn. (3.3) involving $(\omega \ell_0/v)^2$ alone is usually of greater importance .

These considerations lead to our principal conclusion that inclusion of elastic scattering will not significantly alter the calculated cross sections for excitation under normal circumstances.

IV THE PSEUDOPOTENTIAL FOR ALKALI ATOMS

a. Qualitative Justification.

In the alkali atoms one valence electron moves mostly outside a compact core of electrons (in closed shells) which are fairly inactive and this enables us to look at the atoms as one-electron atoms, i.e. we assume that in atomic interactions it is only the valence electron that contributes to the interaction. Nevertheless, the problem is still quite complicated because the presence of these inactive electrons requires that the wave function of the valence electron be orthogonal to the wave functions of electrons in closed shells. The result is that the valence electron wave function must vary rapidly near the nucleus. We are thus faced with an unpleasant situation. We have ignored the presence of the electrons in closed shells and yet (in interactions in which only the valence electron is of interest) we still have to include the effects of the core-electrons wave functions. Is there a way out of this dilemma? Is there a way to remove the effect of the core-electrons wave functions from the problem? This is accomplished by the pseudopotential.

Let us make the following observation. The energy of the lowest state of an electron in a $-e^2/r$ potential, that is, the Hydrogen atom, is -13.6 eV. Compare this with the energy of the lowest state of the valence electron of any of the alkali atoms. In the case of sodium, for example, it is -5.12 eV. This tells us

that the valence electron of sodium is much less tightly bound to the nucleus than the electron in the Hydrogen atom.

right away that the effect of the compact ionic core is a repulsion on the valence electron. This repulsive effect may be attributed to the requirement that the valence electron wave function be orthogonal to the wave functions of the core electrons which, requirement, gives rise to additional kinetic energy of the valence electron when it is inside the core.

We are thus led to represent the potential energy, $V(r)$, of the valence electron by an expression of the form

$$V(r) = -\frac{e^2}{r} + F(r)$$

where $F(r)$ is a repulsive potential. The requirements to be satisfied by $V(r)$ are that it reproduces the known energy levels of the free atom which are determined from spectroscopic data and, for large distances from the nucleus, the valence electron is described by a coulomb wave function.

b. Formulation of the Pseudopotential Method

In this section we present briefly a formulation of the Pseudopotential Method as originally developed by Phillips and Kleinman¹⁵.

We begin by imagining that we know the 'exact' wavefunction for a valence electron in atomic state n . Denote it by $\psi_n(r)$. Denote the wave functions for core states by $\psi_c(r)$. Our aim is to obtain a pseudo wave function, $\Phi_n(r)$, for the valence electron that will be the 'smooth' part (no radial nodes) of $\psi_n(r)$. To this end write

$$\psi_n(r) = \bar{\Phi}_n(r) + \sum_c a_{nc} \psi_c(r) \quad (4.1)$$

The sum extends over all core states. The requirement that $\psi_n(r)$ be orthogonal to all core states $\psi_c(r)$, i.e.

$$(\psi_c, \psi_n) = 0 \quad (4.2)$$

gives

$$a_{nc} = -(\psi_c, \bar{\Phi}_n) \quad (4.3)$$

so that (4.1) becomes

$$\psi_n(r) = \bar{\Phi}_n(r) - \sum_c (\psi_c, \bar{\Phi}_n) \psi_c(r) \quad (4.4)$$

At this point we assume that ψ_c and ψ_n are eigenfunctions of the same Hamiltonian, H , with eigenvalues E_c and E_n , respectively.

$$H \psi_c = E_c \psi_c \quad (4.5a)$$

and,

$$H \psi_n = E_n \psi_n \quad (4.5b)$$

To obtain an equation satisfied by $\bar{\Phi}_n$, substitute (4.4) into (4.5b) and use (4.5a) to get

$$H \bar{\Phi}_n - \sum_c (\psi_c, \bar{\Phi}_n) (E_c - E_n) \psi_c = E_n \bar{\Phi}_n$$

Write the Hamiltonian as $H = T+V$, where V is the real potential, and use it to reduce the above equation to

$$(T+V_p) \bar{\Phi}_n(r) = E_n \bar{\Phi}_n(r) \quad (4.6a)$$

where

$$V_p \Phi_n(r) \equiv V \Phi_n - \sum_c (E_c - E_n) (\psi_c, \Phi_n) \psi_c(r) \quad (4.6b)$$

V_p is the desired pseudopotential, and (4.6a) is the desired equation satisfied by the pseudo wave function Φ_n . Let us rewrite (4.5b), with $H = T+V$, to get

$$(T+V) \psi_n(r) = E_n \psi_n(r) \quad (4.7)$$

Notice the very important comparison between (4.7) and (4.6a). In order to go from the 'exact' wave equation to (4.6a) we replace the real potential V by the pseudopotential V_p and the 'exact' wave function ψ_n by the pseudowave function Φ_n , but retain the same eigenvalue.

Let us look at (4.6a) in a little detail. It is evident that V_p is an energy-dependent non-local operator and so (4.6a) becomes an integro-differential equation whose solution must be obtained self consistently. We want to try to avoid this laborious task. Divide both sides of (4.6b) by Φ_n . The resulting term ψ_c / Φ_n we approximate by the simple function $e^{-\beta r}/r$, a form easily suggested if one approximates ψ_c and Φ_n by Slater orbitals. As for the energy difference $(E_c - E_n)$ one could probably replace it by some average which would not be a poor approximation if variations of $(E_c - E_n)$ were small enough to be neglected.

To avoid all the above we will adopt the Hellmann type pseudopotential¹⁶.

$$V_p(r) = -\frac{e^2}{r} + Q e^{-\beta r}/r \quad (4.8)$$

The pseudopotential parameters Q and β introduced above are, in effect, a measure of the strength and range of the repulsive part of the potential, respectively. They pertain to the specific free atom one is interested in and will have to be determined from spectroscopic data. (From here on we drop the subscript p from V_p).

This same form of the pseudopotential has been applied to other molecular problems by Preuss¹⁷, to the calculation of ground state energies of complex atoms^{18,19}, and to problems in solid state physics²⁰⁻²³. Other forms of the pseudopotential also exist. Ashcroft²⁴ has used the form

$$V(r) = -\frac{Ze^2}{r} \quad r > R_{\text{core}}$$

$$\sim 0 \quad r < R_{\text{core}}$$

where R_{core} is some effective core radius, essentially the ionic radius, and has used it for calculations of resistivities, phonon spectra and phase shifts in alkali metals. Zapol et.al.²⁵ have used a similar form which is continuous within certain ranges of r ,

$$V(r) = -\frac{A_i}{r} \quad R_i \leq r \leq r_{i+1} \quad (i=0,1,\dots,k)$$

to calculate energy spectra and oscillator strengths for monovalent atoms. The arbitrary parameters in the potential were determined by requiring that some of the eigenvalues coincided with the known experimental ones. A different type of pseudopotential, based on the Thomas-Fermi model, proposed by Gombas²⁶ in his recent discussion of the subject of pseudopotentials in atomic systems has been

applied by Bayliss²⁷ for calculating approximate interatomic potentials for ground and low-lying excited states of diatomic systems of alkali-metal noble gas atoms. In closing this section let us point out that in using our freedom for the choice of the repulsive part of the pseudopotential our expression has the advantage of simplicity (with respect to Gombas), continuity (with respect to Zapol et al.) and is simply related to the basic derivation. It does have the disadvantage of being strong and rapidly varying in the core region, which means that care must be taken in numerical work, as we shall see.

c. Determination of the Pseudopotential Parameters

The units employed are: $e^2 = 2$, $m = \frac{1}{2}$, $\hbar = 1$ (energy unit = 1 Ryd.)

The expression for the pseudopotential, (4.8), is

$$V(r) = -\frac{2}{r} + Q \exp(-\beta r)/r \quad (4.9)$$

and the parameters to be calculated are Q and β . This is to be done for sodium and cesium. We will treat the sodium case in detail and give only the results for cesium. This will make the procedure used more specific and understandable.

The sodium atom in its ground state has the 1s, 2s, and 2p shells filled. Its valence electron is in the 3s state. Let us see how the variational method can be used. Denote the (properly normalized) radial parts of the valence electron wave functions for the 3s and 3p states, respectively, by

$$R_{3s}(r) = (\epsilon_1^3/\pi)^{\frac{1}{2}} \exp(-\epsilon_1 r)$$

$$R_{3p}(r) = (\epsilon_2^5/3\pi)^{\frac{1}{2}} r \exp(-\epsilon_2 r)$$

with (known) eigenvalues E_{3s} and E_{3p} . Write the Schrodinger equation for these two states using (4.9) and calculate E_{3s} and E_{3p} in terms of ϵ_1 and ϵ_2 (and also Q and β). The condition that the energy be a minimum requires $\partial E_{3s}/\partial \epsilon_1 = 0$ and $\partial E_{3p}/\partial \epsilon_2 = 0$. This gives enough equations to solve for Q and β .

The unquestioned merit of this procedure is that it is straightforward and the algebra involved is very easy to handle specially when the trial wave functions, $R(r)$, are simple. Because of this many authors have been using this procedure. Callaway²² points out, however, that poor approximations to the true wave functions for such a type of pseudopotential do not allow the electron to avoid the strongly repulsive core (as is found to occur when the Schrodinger equation is solved) and the result is a too soft repulsive part of the pseudopotential.

The method we used in the present work goes as follows²³. The radial part of the wave equation is

$$\frac{d^2}{dr^2} \Phi_{nl} + [E_{nl} - V - \frac{l(l+1)}{r^2}] \Phi_{nl} = 0 \quad (4.10)$$

where E_{nl} is the known experimental value for the free atom nl state, and V is the pseudopotential with trial values for Q and β . Far out in the Coulomb region the repulsive part of the pseudopotential

is negligible, that is, $V = -\frac{2}{r}$ and, in this region, the radial wave equation becomes

$$\frac{d^2 P_{n\ell}}{dr^2} + \left[E_{n\ell} + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2} \right] P_{n\ell} = 0 \quad (4.11)$$

The solution to (4.11) we know. It is the expansion

$$P_{n\ell} = r^s e^{-r/s} \sum_m \alpha_{\ell,m} r^{-m} \quad (4.12)$$

where $s = (-E_{n\ell})^{-\frac{1}{2}}$ and the coefficients $\alpha_{\ell,m}$ satisfy the equation

$$\alpha_{\ell,m} = [\ell(\ell+1) - (s+1-m)(s-m)] \alpha_{\ell,m-1} / (2m/s) \quad (4.13)$$

Now, for a prescribed state, say the 3s-state of sodium (i.e. $E_{n\ell} = E_{3s}$, $\ell = 0$), we integrate (4.10) outwards into the Coulomb region (where the wave function is the known P_{3s}) and then vary Q and β until we can reasonably match the logarithmic derivatives of Φ_{3s} and P_{3s} . In practice one holds Q fixed and varies β . However, this set of values (Q, β) is not unique, and one obtains a curve $Q_1(\beta)$, say, in the Q - β plane, for which solutions are obtained.

Let us pause for a moment and ask the question: How can we make the best use of the freedom given to us as to the choice of the parameters (Q, β) from the $Q_1(\beta)$ curve? Well! We will begin, at once, considering interactions between two (alkali) atoms. Even though we assume that the electrons in closed shells remain inert it is not true that

the valence electron will remain in the s state. That is, the one-electron atom will be polarized to some degree and to an extent we can take account of this polarization right now, by allowing the pseudopotential to describe the interaction of the valence e with its parent ion when in its first excited state, the p-state. This we accomplish by repeating the above process (in the case of sodium) for the 3p state resulting in a new, $Q_2(\beta)$, curve. The intersection of the curves identifies a point at which both states are fit by the same potential, and thus specifies the parameters.

For sodium the 3s and the 3p states were used and an intersection of the two $Q(\beta)$ curves was obtained without difficulty. For cesium the 6s and the 6p states were used. No intersection of the $Q(\beta)$ curves was found in this case and a set of parameters from the $Q(\beta)$ curve of the 6s state was chosen arbitrarily. The error produced in the 6p state energy was .016 Ryd or 8.8%. The pseudopotential parameters adopted for the work to follow are listed in table 1. In the case of sodium the results are in good agreement with those of reference 23.

Table 1. Pseudopotential parameters for Sodium and Cesium
The calculated and actual energies for the 3s and 3p states of sodium and the 6s and 6p states of cesium are given

Atom	Q	β	$E_{calc}(s)$	$E_{exp}(s)$	$E_{calc}(p)$	$E_{exp}(p)$
Na	20.43	2.0475	-.3777	-.377726	-.2231	-.223102
Cs	25.00	1.4239	-.2862	-.286181	-.1972	-.181072

In order to make use of existing molecular integral programs, the calculated s-state pseudo wave functions were fit by a linear combination (5 terms) of slater type orbitals, $\chi_n(r, \zeta)$, defined by

$$\chi_n(r, \zeta) \equiv (2\zeta)^{n+\frac{1}{2}} ((2n)!)^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} \quad (4.14)$$

and individually normalized so that

$$\int \chi_n^2(r, \zeta) r^2 dr = 1 \quad (4.15)$$

In each case, we write for the normalized total pseudo wave function

$$\psi = (4\pi)^{-\frac{1}{2}} \sum_{i=1}^5 \alpha_i \chi_{n_i}(r, \zeta_i) \quad (4.16)$$

The expectation value of the free atom Hamiltonian with the analytic pseudo wave function (4.16) along with the slater orbital parameters n_i , α_i , ζ_i are given in table 2.

Table 2.. Slater orbital parameters and energies for Sodium and Cesium. See equations (4.14) and (4.16) for definition of the parameters.

i	<u>Sodium</u>			<u>Cesium</u>		
	n_i	α_i	ζ_i	n_i	α_i	ζ_i
1	1	.162795	.48778	1	.000096	.12008
2	1	-.942629	1.60674	1	-.470277	.75668
3	1	.801495	1.75614	1	.053886	3.21463
4	2	.926946	.65373	2	1.257517	.53765
5	2	.003845	4.57142	2	.132458	2.28540
Energy		-.377625				-.286169

In figure 3 we plot the pseudopotential for sodium, and in figure 4 we plot the corresponding pseudo wave function. Notice that inside the core the pseudo wave function differs from the true valence electron wave function, in that in the case of the lowest valence state, it is nodeless. For the sake of comparison we show in figure 4 a reasonable approximation to the true valence electron wave function for sodium²⁸.

Fig. 3

Fig. 4

V THE HEITLER-LONDON CALCULATION FOR Na-Cs.

The Heitler-London method was developed right after the invention of wave mechanics by Schrödinger, in an attempt to get an approximate solution to one of the simplest many electron problems, the H_2 -molecule²⁹.

Herring and Flicker have shown that the Heitler-London approximation is incorrect at very large interatomic separations where it predicts, erroneously, that the triplet state should lie below the singlet state in H_2 ³⁰. This crossing of the potential energy curves occurs at an interatomic separation $R_c = 49.5 a_0$. In their work, Herring and Flicker were able to obtain an exact asymptotic expression for the singlet-triplet energy difference in H_2 . Their result is proportional to $R^{5/2} e^{-2R}$ with leading corrections of order $O(R^2 e^{-2R})$. In the range of moderately large distances, the leading term in the exact series obtained by Herring and Flicker and the results of the standard Heitler-London calculation are in good agreement. It is not possible to ascertain the accuracy of the Heitler-London method in view of the lack of knowledge of higher terms in the exact asymptotic series.

Two reasons make us believe that we are justified in using the Heitler-London method in our present work. (i)- In the Na-Cs system the wave functions die off much slower than in the H-H problem, and a crossing of the potential energy curves that one might expect would have to occur at extremely large distances, larger than in the case of hydrogen ($R_c = 49.5 a_0$).

(ii)- The region of interest in the Na-Cs system is that of moderately large distances. In view of the preceding observations the Heitler-London method should be accurate in this region and, furthermore, because of (i) this region should extend to very large separations beyond which one would get but negligible contributions.

We have made a Heitler-London calculation of the energies of the lowest singlet and triplet states of the Na-Cs system. Only a brief outline of the calculation will be given here since this is now a standard method presented in various text books³¹.

Denote the sodium and cesium atoms by A and B, respectively, and assign, arbitrarily, electron 1 to atom A and electron 2 to atom B. When the atoms are separated by a distance R, the Hamiltonian for the interacting system is, in the present approximation,

$$\mathcal{H} = H_A(1) + H_B(2) + V_B(1) + V_A(2) + V(1,2) + V_{AB} \quad (5.i)$$

where

$H_A(1) = T(1) + V_A(1)$ is the free Na atom Hamiltonian

$H_B(2) = T(2) + V_B(2)$ is the free Cs atom Hamiltonian

$V_x(i) = -\frac{2}{r_{ix}} + Q_x \exp(-\beta_x r_{ix})/r_{ix}$ is the interaction

between ion x (A or B) and electron i (1 or 2). This is, of course, the pseudopotential and the parameters Q and β are those given in table I.

$V(1,2) = \frac{2}{r_{12}}$ is the Coulomb repulsion between electrons

1 and 2, and

$V_{AB} = \frac{2}{R}$ is the interaction between the two ions. Here we

assume the ions to be spherical and not interpenetrating.

This will be the case for not too small internuclear

distances R .

In figure 5 we show graphically the interacting system for some fixed distance R . Now, recall the pseudo wave function given by equation (4.16) and write it as

$$a(1) \equiv (4\pi)^{-\frac{1}{2}} \sum_{i=1}^5 \alpha_i \chi_{n_i}(r_{1A}, \xi_i) \quad (5.2a)$$

It describes the motion of electron 1 about atom A. Without any confusion and similar meaning as above we may write

$$\begin{aligned} b(2) &\equiv (4\pi)^{-\frac{1}{2}} \sum_{i=1}^5 \beta_i \chi_{n_i}(r_{2B}, \eta_i) \\ a(2) &\equiv (4\pi)^{-\frac{1}{2}} \sum_{i=1}^5 \alpha_i \chi_{n_i}(r_{2A}, \xi_i) \\ b(1) &\equiv (4\pi)^{-\frac{1}{2}} \sum_{i=1}^5 \beta_i \chi_{n_i}(r_{1B}, \eta_i) \end{aligned} \quad (5.2b)$$

All the parameters in (5.2) are defined by equations (4.14)-(4.16), and are found in table 2. (Here we have used different symbols for each atom). The overlap integral, denoted by S , is defined as

FIG. 5

$$S = \langle a(1) | b(1) \rangle \quad (5.3)$$

The normalized singlet, s, and one of the triplet, t, states are described by

$$\Psi_s = [2(1 \pm S^2)]^{-\frac{1}{2}} [a(1)b(2) \pm a(2)b(1)] \quad (5.4)$$

t

The Heitler-London energies for the singlet and one of the triplet levels are

$$E_s = \langle \Psi_s | \mathcal{H} | \Psi_s \rangle \quad (5.5)$$

t

Use of (5.1) and (5.4) in (5.5) yields

$$E_s = \epsilon_o(A) + \epsilon_o(B) + \frac{V_c \pm V_{ex}}{(1 \pm S^2)} \quad (5.6)$$

t

where $\epsilon_o(A)$ and $\epsilon_o(B)$ are the free sodium and cesium atom eigenvalues, respectively, satisfying

$$H_A(1) a(1) = \epsilon_o(A) a(1)$$

$$H_B(2) b(2) = \epsilon_o(B) b(2)$$

and their values are given in table 2. Here V_c and V_{ex} , ordinarily referred to as the coulomb or direct and exchange integral, respectively, are

$$V_c = \langle a(1)b(2) | V_B(1) + V_A(2) + V(1,2) + V_{AB} | a(1)b(2) \rangle \quad (5.7)$$

$$V_{ex} = \langle a(1)b(2) | V_B(1) + V_A(2) + V(1,2) + V_{AB} | a(2)b(1) \rangle \quad (5.8)$$

In table 3 we give the various integrals that arise when (5.7) and (5.8) are evaluated. We use, as closely as possible the notation of reference 31. The evaluation of these integrals is very lengthy, cumbersome, and time consuming, mostly because our wave functions are linear combinations of several terms, (eqn. 5.2). The most difficult are the two centre integrals. One then introduces elliptical coordinates^{32, 33} λ, μ, ϕ as shown in fig. 6.

Then

$$\lambda = (r_A + r_B)/R \quad 1 \leq \lambda \leq \infty \quad (5.9a)$$

$$\mu = (r_A - r_B)/R \quad -1 \leq \mu \leq 1$$

The third coordinate, ϕ , is the angle of rotation about the axis R joining the two atoms. The element of volume in terms of these coordinates is

$$d\tau = (R/2)^3 (\lambda^2 - \mu^2) d\lambda d\mu d\phi \quad (5.9b)$$

In table 4 we give numerical values of the integrals $S, J_B, J_A, K_B, K_A, J', K', K_B', K_A', J_B', J_A'$ defined in table 3, of V_c and V_{ex} defined by equations (5.7) and (5.8), and of E_s and E_t

Table 3. Integrals met in the Heitler-London calculation for Na-Cs.

$\langle a(1) b(1) \rangle = S$	one-electron two-centre overlap
$\langle a(1) -\frac{1}{r_{1B}} a(1) \rangle = J_B$	
	one-electron one-centre coulomb
$\langle b(2) -\frac{1}{r_{2A}} b(2) \rangle = J_A$	
$\langle a(1) -\frac{1}{r_{1B}} b(1) \rangle = K_B$	
	one-electron two-centre resonance
$\langle a(2) -\frac{1}{r_{2A}} b(2) \rangle = K_A$	
$\langle a(1)b(2) \frac{1}{r_{12}} a(1)b(2) \rangle = J'$	two-electron two-centre coulomb
$\langle a(1)b(2) \frac{1}{r_{12}} a(2)b(1) \rangle = K'$	two-electron two-centre exchange
$\langle a(1) \frac{e^{-\beta_B r_{1B}}}{r_{1B}} b(1) \rangle = K_B'$	
$\langle b(2) \frac{e^{-\beta_A r_{2A}}}{r_{2A}} a(2) \rangle = K_A'$	
$\langle a(1) \frac{e^{-\beta_B r_{1B}}}{r_{1B}} a(1) \rangle = J_B'$	
$\langle b(2) \frac{e^{-\beta_A r_{2A}}}{r_{2A}} b(2) \rangle = J_A'$	

given by equation (5.6), as functions of R , as obtained through the use of existing standard molecular integral programs.

FIG. 6

Table 4. Numerical values of the integrals met in the Na-Cs Heitler-London calculation.

R	S	J_B	J_B'	J_A	J_A'	J'	K_B	K_B'
3.00	.81780	-.25900	.01201	-.20923	.00334	.17594	-.19515	.00384
4.00	.74244	-.22379	.00698	-.19451	.00288	.16595	-.16950	.00296
5.00	.65562	-.19089	.00342	-.17558	.00191	.15448	-.14167	.00210
6.00	.56201	-.16355	.00150	-.15617	.00108	.14227	-.11407	.00139
7.00	.46755	-.14181	.00061	-.13844	.00055	.13007	-.08874	.00089
8.00	.37798	-.12465	.00024	-.12318	.00026	.11847	-.06696	.00055
8.50	.33645	-.11744	.00015	-.11648	.00018	.11303	-.05757	.00043
9.00	.29759	-.11099	.00009	-.11037	.00012	.10786	-.04920	.00033
10.00	.22876	-.09996	.00003	-.09970	.00005	.09843	-.03533	.00020
12.00	.12704	-.08333	.0	-.08329	.00001	.08299	-.01721	.00007
14.00	.06590	-.07142	.0	-.07142	.0	.07136	-.00790	.00002
16.00	.03238	-.06250	.0	-.06250	.0	.06248	-.00346	.00001
19.00	.01031	-.05263	.0	-.05263	.0	.05263	-.00094	.0
22.00	.00306	-.04545	.0	-.04545	.0	.04545	-.00024	.0

Table 4 (Contd).

R	K_A	K_A'	K'	V_c	V_{ex}	E_s	E_t	$E_t - E_s$
3.00	-.21580	.00304	.14094	.45068	.18487	-.28295	.13877	.421722
4.00	-.19536	.00282	.11964	.22854	.07097	-.47071	-.31270	.158018
5.00	0.16910	.00230	.09107	.10055	.01177	-.58523	-.50809	.077146
6.00	-.14017	.00173	.06531	.03819	-.01041	-.64268	-.59276	.049920
7.00	-.11177	.00124	.04426	.01206	-.01434	-.66566	-.63001	.035650
8.00	-.8620	.00085	.02836	.00266	-.01158	-.67160	-.64718	.024415
8.50	-.7487	.00070	.02224	.00082	-.00958	-.67167	-.65207	.019599
9.00	-.06460	.00057	.01722	-.00010	-.00765	-.67091	-.65551	.015399
10.00	-.04726	.00040	.00996	-.00059	-.00449	-.66863	-.65967	.008952
12.00	-.02394	.00016	.00264	-.00029	-.00184	-.66590	-.66222	.003683
14.00	-.01132	.00006	.00067	-.00008	-.00045	-.66432	-.66342	.000895
16.00	-.00513	.00002	.00015	-.00002	-.00010	-.66391	-.66371	.000194
19.00	-.00146	.00001	.00001	-.000001	-.00001	-.66380	-.66378	.000017
22.00	-.000	.0	.0	.0	.0	-.66379	-.66379	.000001

The energies of the singlet and triplet states, and their difference are shown in fig. 7. The singlet state shows a shallow minimum at $r = 8.3 a_0$ whose depth is 0.008 ry (0.109 eV). The triplet state has no minimum in the Heitler-London calculation; however, if a Van der Waals attraction of the form $V_{VDW} = -c/R^6$ is added, a minimum is found. The Van der Waals constant c has been deduced from scattering measurements to have the value $c = 3.014 \times 10^3 \text{ ry}^6 a_0^6$. The minimum in the triplet state energy occurs at $R = 15.8 a_0$, and has a depth of $1.0 \times 10^{-4} \text{ ry}$ (.0013 eV). It is not possible to determine the effect of the Van der Waals interaction on the minimum in the singlet state since the simple expression is not valid at that distance.

Dalgarno and Rudge³⁵ have derived a simple formula for the energy difference between singlet and triplet states at large atomic separations, which they have applied to alkali metal atom pairs. Their formula is

$$E_t(R) - E_s(R) = 2\pi S(R) \Phi(R/2) \psi(R/2) \quad (5.10)$$

where S is the overlap integral, Φ is the wave function for the valence electron bound to one atom and ψ refers to the other atom. These functions are approximated in their paper by the leading term in the asymptotic series for a coulomb potential. Since a number of assumptions are involved in their treatment, it should be noted that for H_2 , the Dalgarno-Rudge formula constantly underestimates

Fig. 7

the energy difference between these states by 20 to 30% at moderately large atomic distances not only with respect to the Heitler-London results, but also with regard to the asymptotic formula of Herring and Flicker³⁰ and the variational calculation of Kolos and Wolniewicz.³⁶ Consequently, its use in the spin exchange calculations is open to some question, although it appears from this work that the error in the cross section is not large. When (4.1) is evaluated using four term asymptotic coulomb wave functions for Na and Cs it gives a smaller energy difference than is yielded by the Heitler-London calculation by about 10 to 20% in the range of distances important in the spin exchange problem. However, if errors of this magnitude can be tolerated, the Dalgarno-Rudge formula is quite convenient since overlap integrals are much easier to compute than two electron coulomb and exchange integrals. The result of the Dalgarno-Rudge computation is compared with the present result in fig. 7.

The present results do not agree well with indications from experimental scattering measurements that the minimum in the triplet state potential energy curve occurs in the vicinity of $9a_0$.^{37,38} The present experimental results are summarized in table 5. The reason for the discrepancy in the triplet state is not known, and appears to be difficult to determine, since the Heitler-London calculation should be accurate at this distance.

Table 5. Position of minimum and binding energies for singlet and triplet states of the Na-Ce system

	$E_s^m(\text{ry})$	$r_s^m(a_o)$	$E_t^m(\text{ry})$	$r_t^m(a_o)$
Neumann and Pauly (ref. 38)	5.07×10^{-2}	4.91	1.25×10^{-3}	9.3
Pritchard et al. (ref. 37)			1.96×10^{-3}	8.55
Present work	8.0×10^{-3}	8.28	1.0×10^{-4}	15.8
Dalgarno and Rudge (ref. 35)			$.98 \times 10^{-4}$	15.8

VI SPIN EXCHANGE CROSS SECTIONS FOR Na - Cs

Denote, as before, the sodium and cesium atoms by A and B, respectively. Let the spin l of ion A be coupled to the spin of the valence electron to form a resultant total spin F . That is, F is the total spin quantum number of atom A before the collision. We are interested in the process in which the total spin of atom A is changed to F' such that $F' \neq F$. This is accomplished by flipping the spin of its valence electron. If, for example, A denoted a H-atom, we would have the process $F = 1 \rightarrow F' = 0$ or the reverse process $F = 0 \rightarrow F' = 1$.

A quantum formulation of the problem was given by Dalgarno³⁹ for H-H collisions and attempts to improve approximate calculations within this formulation followed^{40,41}. The quantal formulation was subsequently extended to include other more complex systems^{35,42}, including most alkali metal pairs. Dalgarno and Rudge³⁵ obtain for the total spin change cross section, which is what one would observe in an actual experiment,

$$Q(F, F') = \frac{\pi(2F' + 1)}{2k^2(2l+1)} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2(\eta_{\ell}^s - \eta_{\ell}^t)$$

where k is the wave number of relative motion, and η_{ℓ}^s and η_{ℓ}^t are the singlet and triplet phase shifts. A reduced spin exchange cross section, Q_{ex} , independent of F' and l can be defined by the equation

$$Q_{ex} = \frac{\pi}{2k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2(\eta_{\ell}^s - \eta_{\ell}^t) \quad (6.1)$$

so that

$$Q(F, F') = \frac{(2F' + 1)}{2(2F + 1)} Q_{\text{ex}}$$

In heavy particle collisions the number of phase shifts contributing to the cross section is large, and we employ the semi-classical approximation which consists in replacing the summation in (6.1) by an integral over impact parameters p , where $kp = \ell + \frac{1}{2}$, and in using the JWKB approximation¹⁴ to evaluate the phase shifts. The expression for the reduced cross section then becomes

$$Q_{\text{ex}} = 2\pi \int_0^\infty p \sin^2 \left\{ \frac{1}{v} f(p) \right\} \quad (6.2)$$

where

$$f(p) = \int_0^\infty \frac{E_t(R) - E_s(R)}{(1 - p^2/R^2)^{\frac{1}{2}}} dR \quad (6.3)$$

and v is the relative velocity of the colliding atoms. Detailed calculations show that the semi-classical approximation is satisfactory in the case of H-H collisions.^{40,41} For E_t and E_s we will use our results from the previous section. The region of interest is that of fairly large interatomic separations and in this region the difference between the triplet and singlet potential energies is very satisfactorily given by the analytic expression

$$E_t(R) - E_s(R) = AR^5 \exp(-\alpha_o R) \quad (6.4)$$

with

$$A = 0.007925$$

$$\alpha_o = 1.0983$$

This expansion is an empirical fit rather than an asymptotic expansion of the integrals. We insert (6.4) into (6.3) and obtain

$$f(Z) = A(Z/\alpha_o)^6 \int_1^\infty \frac{t^6 e^{-Zt}}{(t^2-1)^{\frac{1}{2}}} dt \quad (6.5)$$

where the substitutions

$$\frac{R}{p} = t, \quad Z = \alpha_o p$$

have been made. The integral can be evaluated in terms of Modified Bessel Functions. The algebra, though a little lengthy, is straightforward and gives the result

$$f(Z) = A(Z/\alpha_o)^6 \{ (K_6 + 6K_4 + 15K_2 + 10K_0)/32 \} \quad (6.6)$$

Let $\delta(Z) = \frac{1}{v} f(Z)$; then use of this and (6.6) in (6.2) gives for the cross section

$$Q_{ex} = (2\pi/\alpha_o^2) \int_0^\infty Z \sin^2 \delta(Z) dZ \quad (6.7)$$

We evaluate (6.7) in the following way. First we calculate $f(Z)$, or for a given value of initial relative velocity ν , $\frac{1}{\nu} f(Z)$. For not too large values of Z , $\delta(Z)$ is quite large and $\sin^2 \delta(Z)$ oscillates rapidly. For large values of Z , $\delta(Z)$ goes uniformly to zero as $Z \rightarrow \infty$ and so does $\sin^2 \delta(Z)$. We break up the integral (6.7) into two parts:

$$Q_{\text{ex}} = (2\pi/\alpha_0^2) \left\{ \int_0^{Z_0} Z \sin^2 \delta(Z) dZ + \int_{Z_0}^{\infty} Z \sin^2 \delta(Z) dZ \right\}$$

Z_0 is chosen by actually looking at the function $\sin^2 \delta(Z)$, and it is that value such that for $Z < Z_0$, $\sin^2 \delta(Z)$ oscillates rapidly between values of zero and one so that we can replace it by its average value of $1/2$. The second term is integrated numerically by actually calculating the modified Bessel Functions entering $\delta(Z)$ through (6.6). In all cases the Z_0 chosen was a little smaller than the value of Z for which $\sin^2 \delta(Z)$ ceases to oscillate. (This occurs when the phase δ first attains the value of $\pi/2$). Values of Z_0 ranged between $15a_0$ and $12a_0$, slowly decreasing with increasing relative velocity. It is, therefore, the region of interatomic separations of about $12a_0$ and greater that are significant in the problem and here the analytic fit to $E_t - E_s$ given by (6.4) is very good.

It is convenient to characterize the relative velocity by an effective temperature T defined through

$$\frac{1}{2} \mu \nu^2 = KT \quad (6.8)$$

where μ is the reduced mass of the colliding pair and K is Boltzmann's constant. In fig. 8 we show the behaviour of the phase shift, δ , and $\sin^2 \delta$ as functions of Z for a speed corresponding to a temperature of 500 °K.

Firsov⁴³ has suggested the following approximation to Q_{ex} given by (6.2).

$$Q_{ex} = \frac{1}{2} \pi p^{*2} \quad (6.9)$$

where p^* is that value of p for which

$$\delta(p^*) = 1/\pi \quad (6.10)$$

This approximation has been extensively used to avoid numerical integrations. It is interesting to check the accuracy of this method. In the present case Firsov's approximation predicts a cross section of $1.46 \times 10^{-14} \text{ cm}^2$ for a relative velocity of $6.51 \times 10^4 \text{ cm/sec}$. This is lower than our result for the same velocity by less than 3%. The reduced spin exchange cross sections calculated for collisions of Na and Cs through equation (6.7) are given in table 6.

Using (6.8) as the defining equation for T we can then obtain the following approximate analytic expression for Q_{ex} vs. T .

$$Q_{ex} = a - b \ln T \quad (6.11)$$

with T measured in degrees Kelvin. The constants a and b were found to be

$$a = 2.106, \quad b = 0.100$$

Fig. 8

Table 6. Reduced spin exchange cross sections for Na - Cs collisions as a function of relative velocity.

relative velocity		cross sections
(in $^{\circ}\text{K}$)	(in cm/sec)	(in units of 10^{-14} cm^2)
50	2.06×10^4	1.72
100	2.91	1.65
200	4.12	1.58
300	5.05	1.54
400	5.82	1.51
500	6.51	1.49
600	7.14	1.47
700	7.71	1.45
800	8.24	1.44
900	8.74	1.43
1000	9.21	1.42
1200	10.09	1.40
1500	11.28	1.38
3000	15.95	1.31
10000	29.13	1.20

in units of 10^{-14} cm^2 .

The normalized Maxwellian distribution of the relative velocities of the colliding particles is

$$\mathcal{M}(v) = (\mu/2\pi K\theta)^{3/2} e^{-\frac{1}{2}\mu v^2/K\theta} \quad (6.12)$$

where θ is the temperature of the system. We calculate an effective cross section, Q_{eff} , defined by

$$Q_{\text{eff}} = \int \mathcal{M}(v) Q_{\text{ex}}(v) d^3v \quad (6.13)$$

The calculation is straightforward and yields

$$Q_{\text{eff}} = a - b (2 - \ln(4\gamma/\theta)) \quad (6.14)$$

where $\ln \gamma = .57722$ is Euler's constant. In fig. 9 we plot Q_{eff} as a function of the temperature θ of the system.

Fig. 9

VII SUMMARY AND CONCLUSION

The empirical pseudopotential method provides us with a practical means of treating a many-electron problem. It is simple enough to be used in calculations, and, when the pseudopotential parameters are determined from the free atom energy levels by numerical integration of the wave equation rather than through any simplified variational method, it reproduces fairly accurately the free atom spectroscopic data. Having calculated the pseudopotential for sodium and cesium, we have used it in a Heitler-London calculation to obtain potential energy curves for the lowest singlet and triplet levels of the Na - Cs system. The resulting energy curves were in turn used to calculate spin exchange cross sections.

The effects of elastic scattering, (deviations from straight line trajectory), by a Van der Waals potential, have been considered and our principal conclusion is that inclusion of elastic scattering will not significantly alter the calculated cross sections for excitation under normal circumstances.

It will probably be worthwhile to use the pseudopotential for calculations of potential energy curves associated with homopolar molecules and then obtain macroscopic properties of the gas (e.g. viscosities, virial coefficients, etc.) which can be compared with experimental results which are abundant. This comparison will tell how good the potential energy curves are, and in turn, serve as a measure of the accuracy of the pseudopotential.

In addition, it has become recently possible with crossed beams experiments to make direct measurements of differential scattering cross sections. This, then, would be interesting to formulate theoretically.

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EXAMINATION AND THESIS REPORT

Candidate: Panayiotis Sophocleous Laghos

Major Field: Physics

Title of Thesis: Application of the Pseudopotential Method to
Atomic Scattering

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

May 12, 1969