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Application of the Pseudopotential Method to Atomic Scattering

J. Callaway and P. S. Laghos
Department of Physics, Louisiana State University, Baton Rouge, Louisiana 70803

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The empirical pseudopotential method is discussed and applied to a calculation of the spin-exchange cross section in collisions of Na and Cs atoms. The difference between potential energy curves for the lowest singlet and triplet states of the Na-Cs system is calculated by the Heitler-London method, using a Hamiltonian in which the effects of tightly bound electrons are replaced by a pseudopotential. Wave functions for the free atoms are found by numerical integration using the pseudopotential, and agree well with the exact valence-electron functions at large distances. The scattering phase shifts are calculated in the WKB 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 1.5×10^{-14} cm^2.

I. INTRODUCTION

Knowledge of interatomic forces is of great importance for many problems in astronomy, physics, and chemistry. If the interacting atoms contain only a few electrons, reasonably accurate calculations from first principles are possible. In the case of heavy atoms, some simplifications must be introduced. The objective of the present work is to apply the pseudopotential method, which has been extensively used in solid-state physics to the calculation of the interactions of heavy atoms. Substantial simplifications result. The method is then applied to the interaction of Na and Cs atoms, and, in particular, to the calculation of the spin-exchange cross section.

The general concept of the pseudopotential method can be explained qualitatively with reference to an example; to be specific, consider Na. Frequently, one thinks of Na as an one electron atom even though it contains 11 electrons. The idea of an one-electron system is reasonably legitimate, since under usual circumstances the electrons in the closed $1s$, $2s$, and $2p$ shells are inert. However, their presence greatly complicates calculations, because the wave function of the active, $3s$ electron must be orthogonal to the wave functions of electrons in closed shells, and consequently must vary rapidly near a nucleus. It becomes necessary to include core wave functions in many calculations in which only the valence electrons are of real interest. In the atomic interaction problem, one must include the interaction between the valence electrons on one atom and the core electrons on the other. It is greatly desirable to simplify such calculations by removing the core electrons from the problem. This is accomplished by the pseudopotential.

To see how this is possible, we note that the effect of the core electrons on the valence electron is repulsive. In Na, the energy of the lowest state of the valence electron is -0.378 Ry, compared to the value of -1.0 Ry which would be obtained in the Coulomb field of a single positive charge. The repulsion may be attributed to the requirement of orthogonality, which introduces additional kinetic energy into the wave function.

The pseudopotential which we employ consists of the ordinary potential of a single positive charge $(-2/r)$ plus a short-range repulsive potential which, for convenience, may be taken to be of the Yukawa form

$$V_p(r) = -2/r + (Qe^{-\beta r})/r \ . \qquad (1.1)$$

This potential was introduced by Hellman who considered the molecules K_2 and KH.[1] It has been applied to the calculation of the ground-state energies of complex atoms,[2, 3] to other molecular problems by Preuss[4] and by Szasz and McGinn,[5] and to problems in solid-state physics.[6–8] Other forms of pseudopotentials exist, and will be discussed in Sec. II.

The parameters Q and β of the repulsive part of the potential are determined by requiring that the energies of the lowest two states in the potential V_p agree with the lowest two valence-electron states in the free atom ($3s$ and $3p$ in the case of Na). The actual wave function of a valence electron in the atom outside the core of closed shells is determined (apart from normalization) by its energy and the fact that the potential is Coulombic in this region. Consequently, the wave function produced by V_p (which we will call the pseudo wave function) will agree with the true wave function in this region, except for normalization. However, the normalization will not be badly off, since the volume of the core of closed shells is small compared to the volume over which the valence wave function extends. Inside the core, the pseudo wave function will differ from the true valence-electron wave function, since, in the case of the lowest valence state, the pseudo wave function will be nodeless. The good agreement between the pseudo wave function and (a reasonable approximation to) the true valence wave function for Na is shown in Fig. 1.[9] Beyond the large maximum, the difference amounts to a nearly constant factor of 0.97, a small variation being due to polarization.

The pseudopotential procedure is adopted to the atomic interaction problem in the following way.[1, 4, 5] Consider two alkali-metal atoms A and B, separated by a distance R. The coordinates of the two valence electrons are $\vec{r}_1$ and $\vec{r}_2$. In the present approximation, the Hamiltonian is, in the usual notation,

$$H = T_1 + T_2 + V_p(r_{1A}) + V_p(r_{2B}) + V_p(r_{2A}) + V_p(r_{1B}) + e^2/r_{12} + e^2/R + W_{AB}^{(s)}(R) \ . \qquad (1.2)$$

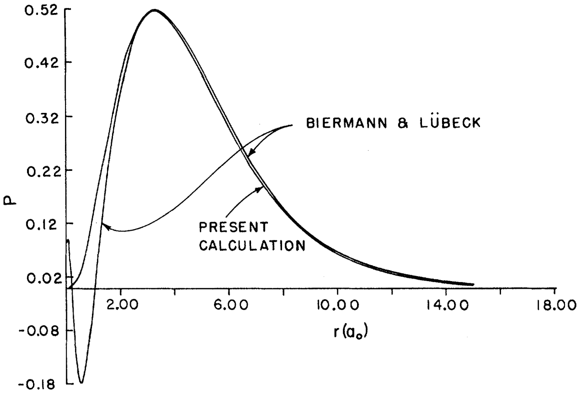

FIG. 1. Radial part P of the pseudo wave function of a valence electron in the Na atom obtained through the use of the pseudopotential is given as a function of radius m atomic units. Included for comparison is a reasonable approximation to the true valence-electron wave function (Ref. 9).

Here, T_1 and T_2 are kinetic energies of the valence electrons. The term $W_{AB}^{(s)}(R)$ is supposed to represent the short-range interaction of the cores of closed shells. Since we will be concerned with the interaction at distances large enough so that the cores do not touch, $W_{AB}^{(s)}$ will be ignored from this point. The resulting Hamiltonian is then available for use in calculating potential-energy curves for the interacting atoms.

II. FORMAL THEORY OF THE PSEUDOPOTENTIAL

Although the pseudopotential method has been in existence for a number of years, we have found that many workers in atomic collisions are unfamiliar with it. Therefore in this section, we review briefly the formal justification for the pseudopotential method, following the original paper of Phillips and Kleinman.[10]

Let the "true" wave function for a valence electron in atomic state n be $\Psi_n(r)$. The wave functions for core states are denoted by $\Psi_c(r)$. We attempt to represent Ψ_n in the form

$$\Psi_n(r) = \phi_n(r) + \sum_c a_{nc} \Psi_c(r) \ . \qquad (2.1)$$

The sum includes all core states. The function ϕ_n is the pseudo wave function which we desire. It is expected to be a smooth function (no radial nodes) near the nucleus. The coefficients a_{nc} are determined by the condition that Ψ_n be orthogonal to all core states:

$$(\Psi_c, \Psi_n) = 0 \ . \qquad (2.2)$$

This gives $a_{nc} = -(\Psi_c, \phi_n)$, so that we have

$$\Psi_n(r) = \phi_n(r) - \sum_c (\Psi_c, \phi_n)\Psi_c(r) \qquad (2.3)$$

An equation for ϕ can be derived by substituting (2.3) into the Schrödinger equation

$$H\Psi_n = E_n \Psi_n$$

It is assumed that Ψ_c is an eigenfunction of the same Hamiltonian as Ψ_n, and that the energy of Ψ_c is E_c. We write the Hamiltonian as $H = T + V$, where V is the actual potential, and obtain an equation for ϕ of the form

$$(T + V_p)\phi_n = E_n \phi_n \ , \qquad (2.4a)$$

where $$V_p \phi_n = V\phi_n - \sum_c (E_c - E_n)(\Psi_c, \phi_n)\Psi_c \ . \qquad (2.4b)$$

V_p is the pseudopotential. It is evident from the form of (2.4b) that the pseudopotential is an energy-dependent nonlocal operator, and that (2.4a) is an integrodifferential equation whose solution must be determined self-consistently. Consideration of the algebraic signs involved in (2.4b) shows that the second term will oppose the first for an attractive V; in other words, that the pseudopotential will tend to be weaker than the true potential.

This expression for the pseudopotential is rather awkward, and it is desirable to replace it by an approximation which is local and energy-independent.[11] To see how this may be done, we note that usually the energy difference $E_c - E_n$ will be reasonably large (of the order of several rydbergs), so that, if our interest is in states in a small range of energies, the variation of $E_c - E_n$ can be neglected, and the term can be replaced by an average. For the dependence on coordinates, we divide (2.4b) by $\phi_n(r)$. It is then convenient to approximate the quantity $\Psi_c(r)/\phi_n(r)$ by a simple function, such as $e^{-\beta r}/r$. This form is suggested if we use Slater orbitals to approximate Ψ_c/ϕ_n.

The result of these arguments is that it should be possible to approximate the nonlocal energy-dependent pseudopotential V_p by $V_p^{(A)}$, where

$$V_p^{(A)} = -2/r + Qe^{-\beta r}/r \ ,$$

which is the expression used in Sec. I. However, it is more desirable to determine Q and β from experimental data than to approximate Eq. (2.4b), and this procedure was, in fact, followed here.

When the pseudopotential procedure is used in calculations of atomic interactions, it is convenient to represent the pseudopotential of the system as the sum of pseudopotentials located on the individual atoms. This will be possible since the core functions Ψ_c will be strongly localized on their individual atoms. Use of the pseudopotential procedure includes the effects of the necessary orthogonality of molecular wave functions for valence states to the core functions on each atom.

It should be noted that the pseudopotential we have used is not unique. Abarenkov and Heine,[12] Ashcroft,[13] and Zapol *et al.*[14] have considered several different forms, which may be discontinuous and contain a nonlocal and energy-dependent part. Gombas has proposed a different type of pseudopotential which is expressed in terms of the electron density,[15] and which has recently been applied by Baylis[16] to alkali-metal–noble-gas interactions. Our expression has the advantage of simplicity (with respect to Gombas), continuity (with respect to Abarenkov and Heine), and a simple relation 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.

Szasz and McGinn[17] have computed pseudopotentials from the Phillips-Kleinman expression (2.4b) for all the alkali metals except Cs, and for a number of other atoms and ions. Their results have been applied to diatomic molecules: Li_2, Na_2, LiH, NaH, and KH. Their calculation is based on the use of Hartree-Fock wave functions for the free atom, and the pseudopotential is evaluated at the free-atom energy. Pseudo wave functions were determined whose energies are in good agreement with ordinary Hartree-Fock calculations. We believe that the procedure used in the present paper has one significant advantage in comparison with the work of Szasz and McGinn for the purpose of calculating the interaction of atoms at large distances: This is that our wave function agrees closely with the asymptotic exact Coulomb wave function at large distances. Since the wave function of Szasz and McGinn has an energy which is close to the Hartree-Fock energy, rather than to the experimental value, their wave function may not be as satisfactory at large distances. It is to be noted that the specific application made here, spin-exchange scattering in the Na-Cs system, is sensitive to the atomic interaction at large distances only.

Two disadvantages associated with this form of pseudopotential deserve comment: (a) Explicit polarization effects are not included. (b) The Phillips-Kleinman pseudopotential depends on the particular state considered, and differs significantly between the 3*s* and 3*p* states in Na for small values of r. The pseudopotential used here is the same for all states. In Na, these effects do not seem to be serious, because a single potential has been found which yields correct values for both the 3*s* and 3*p* states; but in Cs, the difference between *s* and *p* pseudopotentials appears to be important, because no single potential of the form (1. 1), fitting both 6*s* and 6*p* states, could be obtained.

III. DETERMINATION OF THE PSEUDOPOTENTIAL

The pseudopotential parameters are determined by requiring that the energy of the lowest two states in the pseudopotential agree with values obtained from atomic spectroscopy. In the case of Na, the 3*s* and 3*p* levels are involved; in the case of Cs, the 6*s* and 6*p* levels are involved. In the original work of Hellmann, this task was to be accomplished by a variational calculation using simple wave functions whose radial parts are proportional to $e^{-\lambda r}$ for the *s* state, and to $re^{-\nu r}$ for the *p* state. This procedure has been continued by most of the authors who have used this pseudopotential. However, the single simple function of this type is a very poor approximation to the solution of the Schrödinger equation with the pseudopotential. The simple function does not allow the electron to avoid the strongly repulsive core, as is found to occur when the Schrödinger equation is solved. Consequently, the parameters of the repulsive potential, which are reported in the literature from simple variational calculations, are quite inaccurate; basically, the repulsive part of the pseudopotential is too soft.

We performed our calculation by numerically integrating the radial Schrödinger equation for the states of interest. The energy value is prescribed in advance. For a given state, our procedure was to vary the parameters Q and β of the repulsive potential until an eigenstate was obtained for the given energy. Since two parameters are involved the solution is not unique, and one obtains a curve $Q_1(\beta)$, for example, for which solutions are obtained. The process is repeated for the other state, yielding another curve $Q_2(\beta)$. The intersection of the curves identifies a point at which both states are fitted by the same potential, thus specifying the parameters. The process will not work if nonlocal effects are so strong in the atom that a single potential cannot be found which reproduces both states precisely.

For Na, an intersection of the two $Q(\beta)$ curves was found without difficulty. In Cs, no intersection was found, so that parameters were chosen somewhat arbitrarily from the $Q(\beta)$ curve for the 6*s* state. This difficulty is not unexpected for a heavy atom. In this case, the error in the 6*p* energy is 0. 016 Ry or 8. 8%. The pseudopotential parameters finally adopted are listed in Table I. In the case of Na, the results are in good agreement with those of Ref. 8. The pseudopotential for Na is shown graphically in Fig. 2, where it is compared with other pseudopotentials which have been employed elsewhere. The wave function for Na was already shown in Fig. 1.

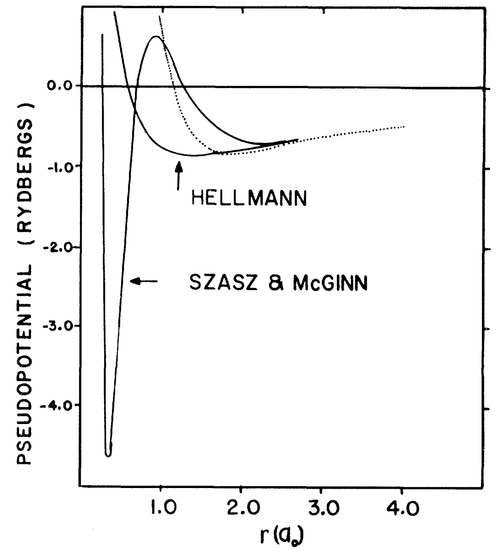

FIG. 2. Pseudopotential for Na. The dotted curve represents our results. The "Hellman" curve is that obtained in Ref. 1. The "Szasz and McGinn" curve is that obtained in Ref. 17, using the Phillips-Kleinman formula (2.4b).

For convenience in performing the molecular calculation to be described in Sec. IV, the calculated *s*-state wave functions were fitted by a linear combination of Slater-type orbitals. This allows the use of existing molecular integral programs. In each case, we write

$$\Psi = (4\pi)^{-1/2}\sum_{i=1}^{5} \alpha_i \chi_{n_i}(\zeta_i, r) . \qquad (3.1)$$

The χ_{n_i} are defined by

TABLE I. Pseudopotential parameters for Na and Cs. The calculated and actual energies for the 3*s* and 3*p* states in sodium and the 6*s* and 6*p* states in Cs are given. All quantities are in atomic units with energies in rydbergs.

Atom	Q	β	$E_{\text{calc}}(s)$	$E_{\text{expt}}(s)$	$E_{\text{calc}}(p)$	$E_{\text{expt}}(p)$
Na	20.43	2.0475	−0.3777	−0.377726	−0.2231	−0.223102
Cs	25.00	1.4239	−0.2862	−0.286181	−0.1972	−0.181072

TABLE II. Slater-orbital parameters and energies (in rydbergs) for Na and Cs. See Eqs. (3.1) and (3.2) for definition of the parameters.

		Na			Cs	
i	n_i	ζ_i	α_i	n_i	ζ_i	α_i
1	1	0.48778	0.162795	1	0.12008	0.000096
2	1	1.60674	−0.942629	1	0.75668	−0.470277
3	1	1.75614	0.801495	1	3.21463	0.053886
4	2	0.65373	0.926946	2	0.53765	1.257517
5	2	4.57142	0.003845	2	2.28540	0.132458
	Energy	−0.377625		Energy	−0.286169	

$$\chi_{n_i}(\zeta_i, r) = (2\zeta_i)^{n_i+1/2}(2n_i!)^{-1/2} r^{n_i-1} e^{-\zeta_i r} \qquad (3.2)$$

and are thus individually normalized so that

$$\int \chi_{n_i}{}^2(\zeta_i, r) r^2 dr = 1 \quad . \qquad (3.3)$$

The coefficients n_i, ζ_i, and α_i are given in Table II. The expectation value of the Hamiltonian for the analytic wave function is also given in Table II. Comparison with the values quoted in Table I indicates that the wave functions are reasonably accurate.

IV. CALCULATION OF POTENTIAL ENERGY CURVES

The calculation of interatomic forces has recently been reviewed by Hirschfelder and Meath.[18] In the present case we are interested in the interaction between Na and Cs atoms at moderately large distances where there is no overlap of the wave functions of core electrons, and the pseudopotential approach should be valid. Moreover, we are interested in spin-exchange scattering which depends in the semiclassical approximation only on the difference in potentials between singlet and triplet states. To the extent that the van der Waals interaction is the same in both singlet and triplet states, its effect may be ignored, and we make this approximation here. Furthermore, since the atomic states involved are *s* states, the angular-dependent part of the van der Waals force will not contribute. Therefore, we propose to calculate the difference in potentials in the Heitler-London approximation using the pseudopotential wave functions described in Sec. III.

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.[19] They have obtained an exact asymptotic expression for the difference between singlet and triplet states in H_2. Their result is proportional to $R^{5/2}e^{-2R}$. However, other terms in the series have not been evaluated. At moderately large distances the leading term in the exact series obtained by Herring and Flicker is in good agreement with the results of the standard Heitler-London calculation, and, in view of the lack of knowledge of higher terms in the exact asymptotic series, it is not possible to ascertain the accuracy of the Heitler-London method. The region of interest in the problem of spin-exchange scattering in the Na-Cs system is that of moderately large distances (where the Heitler-London calculation should be accurate), and it is employed here.

We have made a Heitler-London calculation of the energy differences between singlet and triplet states in the Na-Cs system using the wave functions given by Eq. (3.1), the coefficients being those of Table II. This calculation followed standard methods, and thus need not be described in detail here. The energies of the states, and their differences are shown in Fig. 3. The singlet state shows a shallow minimum at $r = 8.3a_0$ whose depth is 0.008 Ry (0.109 eV.) The triplet state has no minimum in the Heitler-London approximation; however, if a van der Waals attraction of the form $E_{\mathrm{VDW}} = -d/R^6$ is added, a minimum is found. The van der Waals constant c has been deduced from scattering measurements to have the value $c = 3.014\times10^{+3}$ Ry^6 $a_0{}^6$.[20] The minimum in the triplet-state energy occurs at $R = 15.8a_0$, and has a depth of 1.0×10^{-4} Ry (0.0013 eV). It is not possible to determine the effect of van der Waals interactions on the minimum in the singlet state, since the simple expression is not valid at that distance.

Calculations of Szasz and McGinn[17] for alkali-metal diatomic molecules, using the Heitler-London method, employed atomic wave functions which were single Slater orbitals with an exponent which was varied. They obtained about $\frac{1}{3}$ of the observed dissociation energies, and equilibrium separations that were about 25% larger than the experimental results. The present results might be expected to be somewhat better at large distances, because the atomic wave functions are more accurate; however, the adequacy near the singlet minimum is more questionable.

Dalgarno and Rudge[21] have derived a simple formula for energy difference between singlet and triplet states at large atomic separations, which they have applied to alkali-metal atom pairs. Their formula is

$$E_t(R) - E_s(R) = 2\pi S(R)\phi(\tfrac{1}{2}R)\Psi(\tfrac{1}{2}R) \quad , \qquad (4.1)$$

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 Dalgarno and Rudge's 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 consistently underestimates 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 Flicker and the variational calculations of Kolos and Wolniewicz.[22] 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. We have evaluated (4.1) using four-term asymptotic Coulomb wave functions for Na and Cs, and find, in the case of this system also, that the Dalgarno-Rudge formula gives a smaller energy difference than is yielded by our 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 shown in Fig. 3, where it is compared with our result.

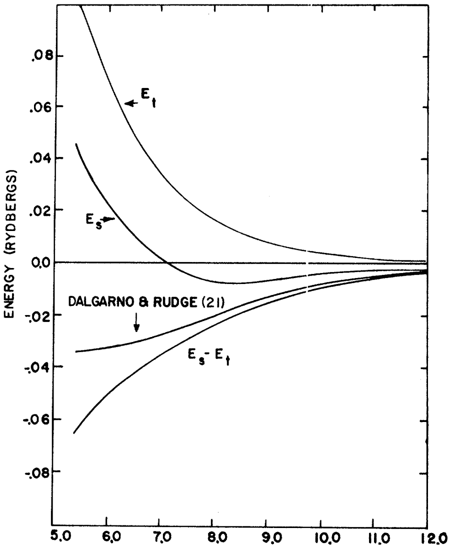

FIG. 3. Heitler-London singlet and triplet potential-energy curves and their differences for Na-Cs. Use of the pseudopotential was made in setting up the interaction Hamiltonian. Included is also the result of the Dalgarno-Rudge formalism (Ref. 21) with four-term asymptotic Coulomb wave functions.

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 9 a.u.[23, 24] The present experimental results are summarized in Table III. The origin of the discrepancy in the triplet state is not certain. The Heitler-London calculation should be accurate at this distance. Furthermore, it seems unlikely that this discrepancy is due to the possible inadequacy of the repulsive part of the atomic pseudopotentials, since the distances involved are quite large compared to the core radius. The difficulties are more probably connected with the van der Waals forces. In this connection, it is interesting to note that Baylis finds, in a study of interactions between alkali-metal and rare-gas atoms, that the long-range force deviates from the simple form proportional to R^{-6} at rather large distances, owing to the importance of high-order induced multipole terms.[16] However, to the extent that such effects are the same in the singlet and triplet states, the spin-ex-

TABLE III. Position of minimum and binding energies for singlet and triplet states of the Na-Cs system.

	E_s^m (a.u.)	r_m^s (a_0)	E_T^m (a.u.)	r_m^T (a_0)
Neumann and Pauly[a]	5.07×10^{-2}	4.91	1.25×10^{-3}	9.3
Pritchard *et al.*[b]			1.96×10^{-3}	8.55
Present work	8.0×10^{-3}	8.28	1.0×10^{-4}	15.8
Dalgarno and Rudge[c]			0.98×10^{-4}	15.8

[a] Reference 24.
[b] Reference 23.
[c] Reference 21.

change calculation is not affected.

V. SPIN-EXCHANGE CROSS SECTIONS FOR Na-Cs

We shall consider the scattering of Na atoms from Cs atoms and in particular the process in which the spin of the Na atom (the spin of its valence electron) is altered. A quantum formulation of the problem was given by Dalgarno[25] for H-H collisions, and attempts to improve approximate calculations within this formulation followed.[26, 27] The quantal formulation was subsequently extended to include other more complex systems,[21, 28] including most alkali-metal pairs.

A reduced spin-exchange cross section was defined by Dalgarno and Rudge to be[21]

$$Q_{\mathrm{ex}}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2(\eta_l^{\,s}-\eta_l^{\,t}) , \tag{5.1}$$

where k is the wave number of relative motion, and $\eta_l^{\,s}$ and $\eta_l^{\,t}$ are the singlet and triplet phase shifts. In heavy-particle collisions, the number of phase shifts contributing to the cross section is large, and we employ the semiclassical approximation, which consists of replacing the summation in (5.1) by an integral over impact parameters p, where $kp=l+1/2$, and then using the JWKB approximation[29] to evaluate the phase shifts. The expression for the reduced cross section then becomes

$$Q_{\mathrm{ex}}=2\pi\int_0^{\infty}p\sin^2\left(\frac{1}{v}f(p)\right)dp , \tag{5.2}$$

where $$f(p)=\int_p^{\infty}\frac{E_t(R)-E_S(R)}{(1-p^2/R^2)^{1/2}}\,dR , \tag{5.3}$$

and v is the relative velocity of the colliding atoms. Detailed calculations show that the semiclassical approximation is satisfactory in the case of H-H collisions.[26, 27]

For E_t and E_S, we will use our results from Sec. IV. 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

$$E_t(R)-E_s(R)=AR^5e^{-\alpha_0R} , \tag{5.4}$$

with $A=0.007925$, $\alpha_0=1.0983$

This expression is an empirical fit rather than an asymptotic expansion of the integrals. We insert (5.4) and (5.3) and obtain

$$f(z)=A\left(\frac{z}{\alpha_0}\right)\int_1^{\infty}\frac{t^6e^{-zt}}{(t^2-1)^{1/2}}\,dt , \tag{5.5}$$

where the substitutions

$$R/p=t,\quad z=\alpha_0p$$

have been made. Equation (5.5) can be expressed in terms of modified Bessel functions. The algebra, though a little lengthy, is straightforward and gives the result

$$f(z)=A(z/\alpha_0)^6[\tfrac{1}{32}(K_6+6K_4+15K_2+10K_0)] . \tag{5.6}$$

Let $\delta(z)=(1/v)f(z)$; then the use of (5.6) in (5.2) gives for the cross section

$$Q_{\mathrm{ex}}=\frac{2\pi}{\alpha_0^{\,2}}\int_0^{\infty}z\sin^2\delta(z)dz \tag{5.7}$$

We evaluate (5.7) in the following way: First we calculate $f(z)$ or, for a given value of initial relative velocity v, $(1/v)f(z)$. For not too large values of z, $\delta(z)$ is very 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 (5.7) into two parts:

$$Q_{\mathrm{ex}}=\frac{2\pi}{\alpha_0^{\,2}}\left(\int_0^{z_0}z\sin^2\delta(z)dz+\int_{z_0}^{\infty}z\sin^2\delta(z)dz\right). \tag{5.8}$$

z_0 is chosen by actually looking at the function $\sin^2\delta(z)$, and it is that value, where for $z<z_0$ $\times\sin^2\delta(z)$ oscillates rapidly between values of zero and one, so that we can replace it by its average value of $\frac{1}{2}$. The second term is integrated numerically by actually calculating the modified Bessel functions entering $\delta(z)$ through (5.6). 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 $\frac{1}{2}\pi$. 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 (5.4) is very good.

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

$$\tfrac{1}{2}\mu v^2=KT ,$$

where μ is the reduced mass of the colliding pair, and K is Boltzmann's constant. In Fig. 4, we show the behavior of the phase shift δ and $\sin^2\delta$ as a function of z for a speed corresponding to a temperature of 500 °K.

Firsov[30] has suggested the following approximation to Q_{ex} given by (5.2):

$$Q_{\mathrm{ex}}=\tfrac{1}{2}\pi p^{*2} , \tag{5.9}$$

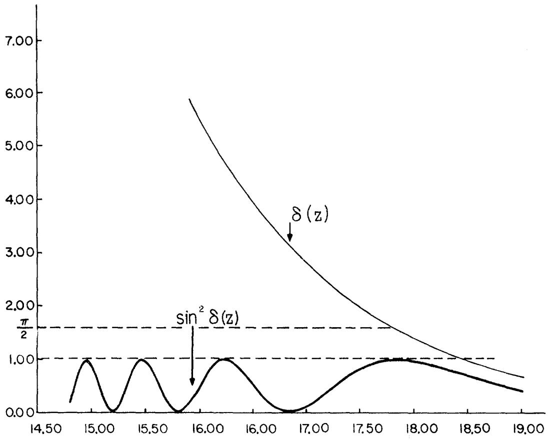

FIG. 4. Behavior of the phase δ and $\sin^2\delta$ as functions of $z(=\alpha_0 p$, where p is the impact parameter) for a relative velocity of 6.5×10^4 cm/sec (500 °K).

where p^* is that value of p for which

$$\delta(p^*) = 1/\pi \quad . \qquad (5.10)$$

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 1.46×10^{-14} cm², for a relative velocity of 6.51×10^4 cm/sec. This is lower, by less than 3%, than what is obtained by solving (5.7) exactly. The spin-exchange cross sections calculated for collisions of Na and Cs through Eq. (5.7) are given in Table IV.

Using (5.8) as the defining equation for T, we can then obtain the following approximate analytic expression for Q_{ex} versus T:

$$Q_{\text{ex}} = a - b\ln T \quad . \qquad (5.11)$$

with T measured in degrees Kelvin. The constants a and b were found to be $a = 2.106$ $b = 0.100$ in units of 10^{-14} cm².

Now, the normalized Maxwellian distribution of the relative velocities of the colliding particles is

$$\mathfrak{M}(v) = (\mu/2\pi k\Theta)^{3/2} e^{-1/2\mu v^2/k\Theta} , \qquad (5.12)$$

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

$$Q_{\text{eff}} = \int \mathfrak{M}(v) Q_{\text{ex}}(v) d^3v \quad . \qquad (5.13)$$

The calculation is straightforward and yields

$$Q_{\text{eff}} = a - b[2 - \ln(4\gamma/\Theta)] \quad , \qquad (5.14)$$

TABLE IV. Spin-exchange cross section for Na-Cs collisions as a function of relative velocity.

Relative velocity (° K)	(10^5 cm/sec)	Spin-exchange cross section (10^{-14} cm²)
50	2.06	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
1 000	9.21	1.42
1 200	10.09	1.40
1 500	11.28	1.38
3 000	15.95	1.31
10 000	29.13	1.20

where $\ln\gamma = 0.57722$ is Euler's constant.

In Fig. 5, we plot Q_{eff} as a function of the temperature Θ of the system.

V. CONCLUSION

The empirical pseudopotential method furnishes a practical means of calculating potential-energy curves for the interaction of heavy atoms at moderate distances. This procedure has been applied here to the interaction of Na and Cs atoms. The present work differs from previous applications of this procedure principally in that the pseudopotential parameters are determined from free-atom energy levels by numerical integration of the Schrödinger equation with the pseudopotential,

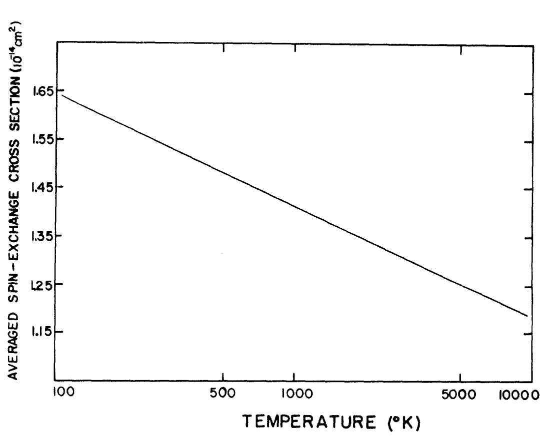

FIG. 5. Thermal average of spin-exchange cross section for Na-Cs as a function of system temperature θ.

rather than through an oversimplified variational technique. The potential-energy curves, here calculated for the lowest singlet and triplet states of the Na-Cs system in the Heitler-London approximation, were applied to the determination of the spin-exchange cross section. The result is a slowly decreasing function of relative speed, whose value at a speed corresponding to 500 °K is approximately 1.5×10^{-14} cm^2.

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