The interpretation of experimental scattering cross sections with pseudopotential calculations for the alkali–mercury interaction

R Düren

Max-Planck-Institut für Strömungsforschung, Böttingerstrasse 4–8, D3400 Göttingen, Germany

Abstract. For the example of collisions of alkali metals with mercury the potentials for the ground-state and the lowest excited states are determined by a comparison of a pseudopotential calculation with experiments. The potentials for Na, K, Rb and Cs are described by one common pair of parameters in the pseudopotential. From this example a new method for the evaluation of scattering data is derived, which should allow a uniform description of the potentials of a class of collision systems.

1. Introduction

Interactions of atoms in electronically excited states can be investigated using molecular-beam techniques in basically two types of experiments: the scattering of ground-state atoms with the observation of the excitation, and the scattering of electronically excited atoms. Experiments of the first type can be performed by observing the light emitted from the excited atom after the collision or by measuring the energy loss of the projectile atom due to the inelastic collision. It is only recently that experiments of the second type have become possible for excited atoms with normal lifetimes (10^{-8} s) using a laser for the excitation.

Both types of experiments, which differ substantially from each other in the experimental set-up, are described by the same set of coupled Schrödinger equations, which with a suitable choice of the basis functions can be written as

$$\Delta_R \psi + \mathbf{U} \psi = E \psi.$$

Here Δ_R is the operator of the kinetic energy of the motion of the nuclei, ψ the wavefunction for the nuclear motion, E the total energy and $\mathbf{U}$ the potential matrix.

The various experimental cross sections derived from this equation can in turn be used for the determination of the potential matrix. In principle all elements of the potential matrix contribute to the values of the cross sections and it is obvious that this complex dependence can only be resolved if a correspondingly large number of experiments is available.

In this situation it seems worthwhile to consider an independent way of determining the potential matrix in a calculation. Obviously problems of size need to be considered here, for example the alkali–mercury interactions are too large for *ab-initio* calculations, but a pseudopotential calculation can be performed.

The advantage of pseudopotential methods is their high computational speed. However, the problem arises that the limits of the model assumed in these calculations are quite uncertain. Therefore a continuous check on the reliability of the calculation by comparison with experimental results is necessary.

On the other hand one can expect to improve the present models on the basis of this comparison and to extend their range of validity to other systems. Especially it should be possible to develop models which apply for specific classes of interactions.

The direction of this work is twofold. Firstly we want to report a pseudopotential calculation for the alkali metals Na, K, Rb and Cs interacting with Hg. The experimental basis of these potentials are the ground-state cross sections. The main result will be that the experimental cross sections included in our analysis are compatible with a pseudopotential which depends on only two parameters and these two parameters are constant for all these systems considered. In these calculations the potentials for the excited states are obtained simultaneously. Therefore a second direction will be that, as far as possible, checks on the potentials obtained with respect to experiments for excitation processes will be considered.

In this context the experiments concerning the alkali–mercury interaction play a special role. For these systems, at present, various reliable experimental results are available. Firstly there are the very accurate measurements of the ground-state interaction (Buck *et al* 1972). For electronic excitation, experiments concerning the threshold of the excitation of the P state from the ground state have been reported (Larsen and Herschbach 1977). The measurement of the integral cross section by a spectrometer analysis of the light has been performed (Moritz 1977). Other experiments will be completed in the near future and qualitative results from these are available: (i) the measurement of the double-differential cross section (Strunck 1977, Schädlich 1977), (ii) the measurement of the total differential cross section for P-state sodium at thermal energies (Düren *et al* 1976, Hoppe 1977).

We will introduce the subject by presenting the calculation in §2. The method and the results for the potentials and the radial coupling elements will be discussed there, concluding with a summary of the common properties of the various systems and their comparison. In §3 we well summarise the experimental results and discuss the comparison between calculated and experimental results. In the summary we will discuss the specific results obtained for the alkali–mercury systems and the general aspects of our method for the interpretation of collision experiments.

The results of the pseudopotential calculation will be given here in general terms and characteristic data as crossing radii etc are provided in tables (table 1 and 2). Listings of the adiabatic potentials and the matrix elements in the diabatic basis are available (Düren 1977b). A short communication has been given previously (Düren 1976).

2. Calculations

2.1. General formulations

The subject of the calculation of the potentials has been reviewed in various articles and will not be repeated here. In the context with the comparison with scattering experiments a few remarks may be sufficient.

Considering the alkali–mercury interaction one first realises that the valence electron may be considered as the only active electron of our system. Therefore a

reasonable choice of basis functions for the expansion of the electronic part of the wavefunction will be given by the alkali wavefunctions. This will immediately guarantee the correct asymptotic behaviour and in this basis the matrix elements for the electronic part of the Hamiltonian H' will be given by

$$U_{ij} = \langle e_i | H' | e_j \rangle$$

where the $|e_i\rangle$ represent the alkali wavefunctions. If the centre of the alkali atom is chosen as the origin, this basis is termed a diabatic basis in the definition of Smith (1969), in that the derivative with respect to the nuclear coordinates will vanish identically. In a scattering calculation the matrix $\mathbf{U}$ will appear as the potential in the Schrödinger equation for the nuclear motion and specific examples of such treatments have been given (Smith 1969, Reid 1973, Mies 1973). In the references it is shown that in this treatment the coupling between the various states is given by only the off-diagonal elements of $\mathbf{U}$.

By diagonalising the matrix $\mathbf{U}$ one obtains the usual (adiabatic) potentials, which we will call $\mathbf{V}$. Using these potentials and the respective wavefunctions in a scattering calculation, the coupling between various states is seen to be confined to the off-diagonal elements for the operator of the kinetic energy of the nuclei (Smith 1969). In detail, these coupling elements can be written in terms of matrix elements for

$$P_{ij} = \langle e_i | \partial/\partial R | e_j \rangle$$

or

$$S = \langle e_i | L_\pm | e_j \rangle$$

where the first type refers to the so-called radial coupling and the second type with step-up/step-down operators $L_\pm$ refers to the rotational coupling.

In principle both basis systems are equivalent but from a practical point of view one or the other may have some advantage.

In a full quantum-mechanical treatment of the scattering the diabatic basis may be preferred. The first reason for this preference is that the matrix elements are obtained in the potential calculation anyway. As a second reason one may note that the Schrödinger equation in this representation is somewhat simpler.

For semiclassical considerations of the scattering process the use of the adiabatic basis may be preferred, basically because one needs a detailed knowledge of the crossing points which can be obtained more easily in the adiabatic basis.

2.2. The calculation of the potentials

2.2.1. The method. The general framework of the calculation has been described earlier (Baylis 1969a,b, Pascale and Vandeplanque 1974) and we follow Baylis's work closely. The major differences between the previous calculations for alkali–rare-gas interactions and the ones for the alkali–mercury interactions presented here can be discussed with reference to the effective interaction potential for the valence electron V_1:

$$V_1(r, R) = F(r, R) + G(r, R) + W(R) \tag{2.1}$$

where r describes the coordinate of the valence electron with respect to the alkali atom. $F(r, R)$ represents the attraction between the valence electron and the dipoles which are induced in the mercury atom by the charges of the electron and the alkali core. $G(r, R)$ describes the repulsion between the valence electron and the electrons

of the mercury atom and $W(R)$ the repulsion between the alkali core and the mercury atom.

Obviously the description of $F(r, R)$ with the induced dipoles breaks down if the charged particles approach the target atom closely and the attractive forces will go to a finite value in the united-atom limit. To approximate this behaviour the induced-dipole expression is assumed to hold outside a sphere with radius r_0 surrounding the mercury atom. Inside this sphere the field is taken equal to the (constant) average value on the surface of the sphere. This leads to

$$F(r, R) = \begin{cases} -\tfrac{1}{2}\alpha_B e^2 \left(\dfrac{R}{R^3} - \dfrac{r'}{r'^3} \right)^2 & \text{for } r' \geqslant r_0 \\[2ex] -\tfrac{1}{2}\alpha_B e^2 \left(\dfrac{1}{R^4} - \dfrac{1}{r_0^4} \right) & \text{for } r' < r_0 \end{cases} \tag{2.2}$$

where we use $r' = R - r$. The radius r_0 of the sphere is used as the first free parameter of the model. As another parameter in the attractive forces (equations (2.2)) we use the polarisability of the target atom. For the alkali–rare-gas interaction the polarisability as determined from experiments has been used (Baylis 1969a,b, Pascale and Vandeplanque 1974). Our choice as a second parameter is suggested by the fact that the induced-dipole approximation is poor at small distances. Higher attractive multipoles should be taken into account as well. For simplicity we retain this first approximation and to compensate for the lack of attraction we choose α_B to be larger than the ones from macroscopic measurements of the polarisability (Wüsthoff 1936).

These two parameters are the only ones of the total interaction potential V_I. In the repulsive contributions no further parameters will be used.

Basically the repulsive interactions are calculated according to the pseudopotential method which has been developed for the calculation of atomic wavefunctions (Gombás 1967). In this method the potential of an electron with respect to an electron density is given by the energy of the next free element in the phase space. Hence this potential can be written with the density ρ of the electrons (Gombás 1967). Specifically one finds for the interaction $G(r, R)$ (Baylis 1969a,b) with the density ρ_B of the target atom

$$G(r, R) = \tfrac{1}{2} m_e [3\pi^2 \rho_B(r')]^{2/3}. \tag{2.3}$$

Integration of this expression over the density of the electron distribution of the alkali core yields the final term

$$W(R) = \frac{3}{10} m_e (3\pi^3)^{2/3} \int \mathrm{d}r \, [\rho_A(r) + \rho_B(r')]^{5/3} - \rho_A^{5/3} - \rho_B^{5/3} \tag{2.4}$$

where ρ_A is the density of the electrons of the alkali core. The densities ρ_A and ρ_B are given as

$$\rho(x) = \frac{1}{4\pi} \sum_s \zeta(s) x^{\alpha(s)} \exp[-2\beta(s)x] \tag{2.5}$$

where the sum is over the occupied shells. The coefficients ζ, α and β have been determined by approximations to SCF densities and are known for the systems considered here (Gombás 1967, Baylis 1969a,b).

For the effective potential V_I described above, the matrix elements are calculated with Bates–Damgaard wavefunctions (Bates and Damgaard 1949) for the free alkali

Hamiltonian. We use as the basis the four lowest states of the alkali atom, which in the asymptotic limit refer to the $^2S_{1/2}$, $^2P_{1/2}$ and $^2P_{3/2}$ states.

In contrast to the alkali–rare-gas calculations (Baylis 1969a,b, Pascale and Vandeplanque 1974) where the density of the rare gas has been described by the outer term of equation (2.5) we use three terms for the mercury atom. This requires some minor changes in the calculation of the matrix elements for $G(r, R)$ and a numerical integration for $W(R)$.

As a basis for our expansion we use the atomic ground state and the lowest P states of alkali atom. The influence of higher order expansion functions has been examined in the alkali–rare-gas case (Pascale and Vandeplanque 1974). The basic result of these investigations is that in the range of internuclear distances smaller than the equilibrium distance of the ground state, the potentials for the ground state and the $A\,^2\Pi$ states are modified by only approximately 0·1 kK, but the $B\,^2\Sigma_{1/2}$ state may show variations of the order of some kK. In the later discussion it will become clear that our experimental findings allow us to neglect the excited states as judged from the respective excitation cross sections. However, a warning concerning the details of the shape of the $B\,^2\Sigma_{1/2}$ state in particular is appropriate.

For the optimisation of the two parameters of the model r_0 and α_B we used as input data the well depth and the equilibrium distance r_m for the ground state interaction of a particular system namely Na–Hg. Specifically r_0 and α_B were varied until the equilibrium data, which are well known from molecular beam studies (Buck *et al* 1972), were matched within the experimental error (see table 1 entry Na–Hg). The parameters are specifically $r_0 = 2\cdot0$ au and $\alpha_B = 70$ au (which is twice the value for the experimental polarisability (Wüsthoff 1936)).

2.2.2. Results for the ground-state interaction.

With the particular choice of r_0 and α_B obtained from the fit the remaining systems K–Hg, Rb–Hg and Cs–Hg were calculated and, in the cases where the experimental values are known, satisfactory agreement between experimental and theoretical results has been obtained (see table 1). The values for Rb–Hg are predicted; for this system experimental values are not available. The error of this prediction is estimated to be less than 5%.

The shape of the ground-state potential in the region of the minimum is in good agreement with the shape determined from the experiment (Buck *et al* 1972). This is demonstrated in figure 1 where the reduced potentials for Cs–Hg are given. It is seen from this figure that the shape is matched reasonably in the range of the minimum. A similar result is shown in figure 2 where the Na–Hg potentials are shown. The dots with the ground-state potential represent the experimental values.

The main point in the results for the ground state seems to us to be the consistency

Table 1. Calculated and experimental results for the ground state interaction.

	Na–Hg[a]	K–Hg	Rb–Hg	Cs–Hg
r_m (calc) (au)	8·80	9·40	9·70	10·05
r_m (exp) (au)	8·92	9·28	—	9·62
ϵ (calc) (kK)	0·446	0·426	0·403	0·380
ϵ (exp) (kK)	0·443	0·423	—	0·404

[a] The entries for Na–Hg are obtained by fitting the experimental and the calculated values.
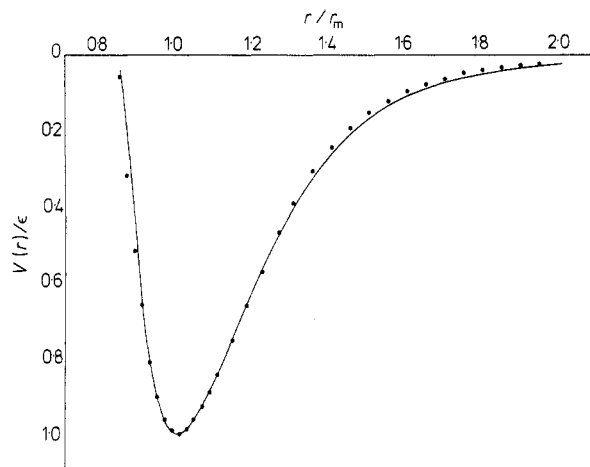
Figure 1. Reduced potential for the ground state of Cs–Hg. Full curve: calculated potential; ●: experimental points.

of the pseudopotentials with one common set of parameters. This reflects an important property of the model. It is flexible enough to describe the properties of Hg which are independent of the alkali atom involved using only the two parameters r_0 and α_B.

2.2.3. Results for excited states and couplings. On the basis of a fit to a particular ground-state interaction the pseudopotential calculation yields the potentials for the excited states and the coupling elements as well as the ground-state potentials of the other systems. In this section we want to demonstrate the typical behaviour of these functions for two specific systems: for Na–Hg at medium and large internuclear distances and for K–Hg at small internuclear distances. A survey of the typical results and the comparison of different systems will be given in the next section. Figure 2 shows the Na–Hg case. The upper part shows the potentials for the ground state and the excited states. The dominant feature of the potentials of the excited states is the avoided crossing of the two states with $m_j = \frac{1}{2}$ which occurs for this special system at 11·35 au. The respective radial coupling element displayed in the lower part of the figure shows a narrow peak at the same position. A second avoided crossing between the same states is found at large internuclear distances in this special example at 20·00 au. Again the respective radial coupling shows a maximum there. The values of the coupling elements at the respective maxima differ by a factor of about 50. In the range of internuclear distances shown in the figure no further couplings occur, in particular one does not find couplings into the ground state.

These couplings occur at smaller internuclear distances for K–Hg as can be seen in figure 3. Here one finds a sequence of avoided crossings where all the states with $m_j = \frac{1}{2}$ are coupled with each other. In the radial couplings maxima are found where the ground state $X\,^2\Sigma_{1/2}$ and the upper states $A\,^2\Pi_{1/2}$ and $B\,^2\Sigma_{1/2}$ are connected. The coupling between the two excited states $A\,^2\Pi_{1/2}$ and $B\,^2\Sigma_{1/2}$ is much narrower and stronger at the maximum. It is noteworthy that it is restricted to a region where the couplings with the ground state are also significant.

The extension of the pseudopotential calculation to such small internuclear distances as are shown in this figure has some problems; the small basis of alkali
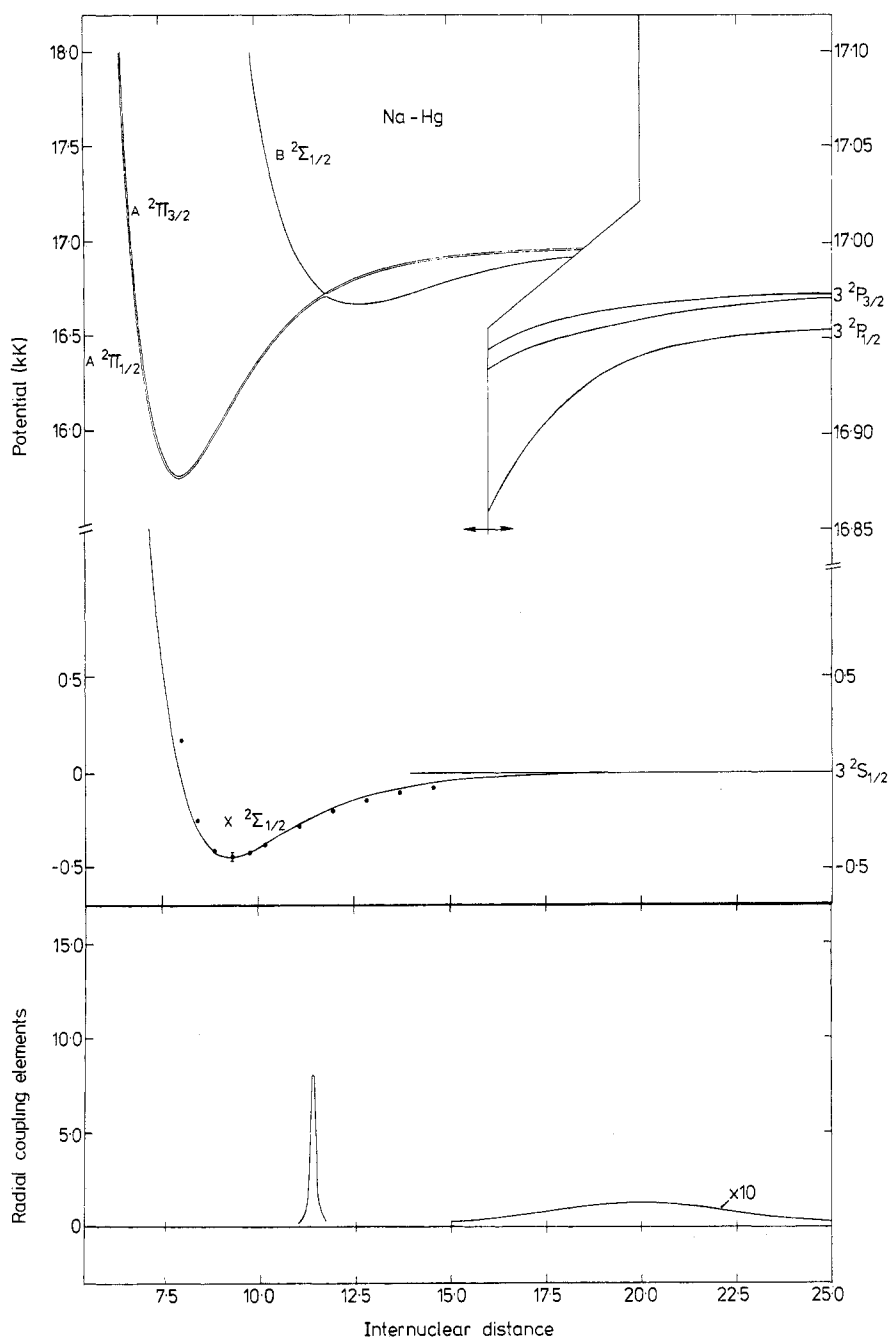
Figure 2. Calculated potentials for Na–Hg. Adiabatic potentials: upper panel; radial coupling elements: lower panel.

wavefunctions used in the expansion and the neglect of possible excited states of mercury, for example. However it will be seen in the final comparison with the experimental findings that these approximations can be justified.
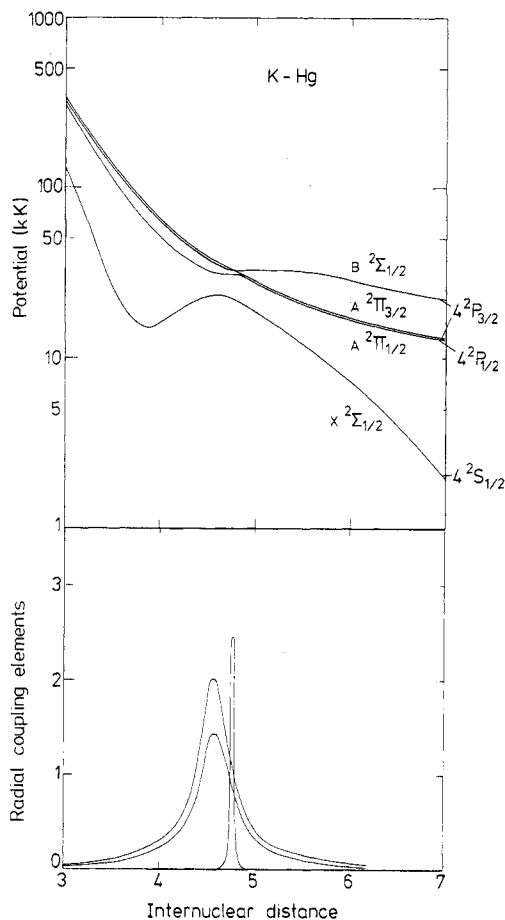
Figure 3. Calculated potentials for K–Hg. Adiabatic potentials: upper panel; radial coupling elements: lower panel.

2.2.4. Discussion. The behaviour of the special systems Na–Hg and K–Hg presented so far is also found for Rb and Cs. Therefore a qualitative survey of all these potentials can be compiled and this is displayed in figure 4. In summary the picture is characterised by four avoided crossings for the $m_j = \frac{1}{2}$ states. At a first crossing radius R_1 the ground state $X^2\Sigma_{1/2}$ couples into the two excited states $A^2\Pi_{1/2}$ and $B^2\Sigma_{1/2}$. The remaining crossings connect only the excited states $A^2\Pi_{1/2}$ and $B^2\Sigma_{1/2}$: the first at R_2 which is close to R_1 and then at larger distances R_3 and R_4. In the intermediate ranges between two crossing points one of the two potentials for the $m_j = \frac{1}{2}$ states is seen to be close to the one for the $m_j = \frac{3}{2}$ state while the other is well separated. The average energies in these crossings $E_1^{(2)}$, $E_1^{(1)}$, E_2, E_3 and E_4 are such that the ones at R_1 and R_2 are well above the asymptotic energy of the P level. Obviously in a collisional-excitation experiment or an experiment with the interaction of the excited atoms a threshold has to be surmounted to make the respective couplings effective. The energies at R_3 and R_4 are below the asymptotic value of the P level which means that these couplings in experiments with excited atoms will be effective for all collision energies.
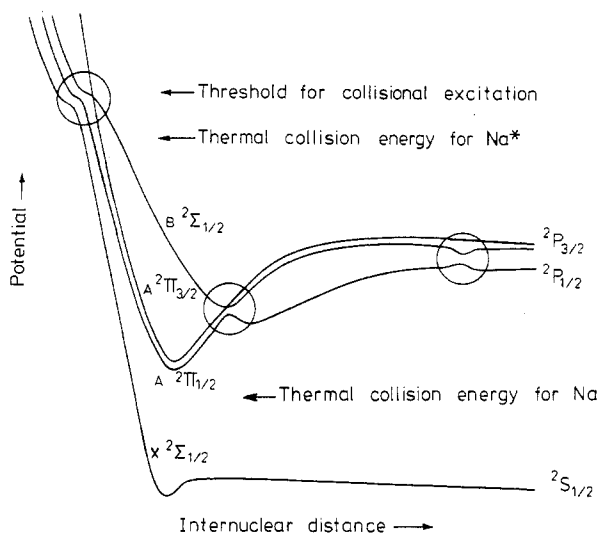
Figure 4. Alkali–mercury potentials: qualitative survey.

In the following systematic analysis of the couplings which have been found we want to investigate the ones involving the ground state and the ones which refer only to the excited states separately. We will try to interpret these cases in terms of physical quantities, which will lead us finally to simple approximate expressions for the localisation of the crossing points.

The couplings for the excited states, very similar to the ones considered here, are known from the alkali–rare-gas interaction. In this context the reason for these couplings is the rearrangement of the angular momentum (Nikitin 1965, Masnou-Seeuws and McCarroll 1974, Wilson and Shimoni 1974). At the different internuclear distances either the spin–orbit interaction in the alkali atom or the molecular interaction dominates. In the first case the total angular momentum and its projection m_j are good quantum numbers. This occurs if the distortion of the level ΔV is smaller than the fine-structure splitting ΔE (Hund's case c). In the second case the angular momentum and the spin decouple and, because of the cylindrical symmetry, m_l and m_s are conserved (Hund's cases b or a) and the molecular interaction is larger than the fine-structure splitting. It will be shown in the following that a sequence of changes between these limiting cases occurs as a function of the internuclear distance and the avoided crossings are found in the transition regions.

To discuss this in some more detail we first need a measure for the orbit–axis interaction. This can be found by neglecting the s–p interaction and the fine-structure splitting (Baylis 1969a,b). Under these simplified circumstances one gets a Σ and a Π molecular state from the p state for which the difference potential represents the orbit–axis interaction (Düren 1977a)

$$V_\Sigma - V_\Pi = \tfrac{3}{5}V_{11}^{(2)}.$$

Here $V_{11}^{(2)}$ is the matrix element of the second dipole moment with the p state.

Before discussing the potentials in terms of this matrix element let us first consider the behaviour of $V_{11}^{(2)}$ as a function of the internuclear distance. Due to the long-range attraction this matrix element will be negative for large internuclear distances. At intermediate distances $V_{11}^{(2)}$ will have a zero, where attractive and repulsive forces

are equal. After that the repulsive forces will dominate until the maximum of the p function coincides with the maximum of the mercury density. For decreasing distance the repulsion will decrease rapidly while the attraction continues to grow, this leads to another zero matrix element.

The position of the zeros will depend on the strength of the interaction and the size of the p function. Since in the cases considered here the interaction is always the same, we will only find the dependence on the size. Going from Na to Cs the zeros will be shifted to larger distances. Obviously a collision in the excited state will always start with Hund's case c. Whether with decreasing internuclear distances one finds one or more transitions into case b will depend on the absolute value of $V_{11}^{(2)}$ in the extrema compared with the fine-structure splitting. Of the systems considered here distinct extrema will be found for Na and K, while they are less pronounced for Rb and Cs.

In the light of these results we can return to the discussion of the avoided crossings between the potentials for the excited states. At large internuclear distances the orbit–axis interaction is less than the spin–orbit interaction, but it increases rapidly (in magnitude) and leads to a transition from Hund's case c to case b. In the potential curve this will be visible as a weak avoided crossing. The corresponding crossing radius R_4 is given by the condition that the orbit–axis interaction equals the fine-structure splitting ΔE:

$$V_{11}^{(2)}(R_4) = \tfrac{5}{3}\Delta E.$$

With decreasing internuclear distances the orbit–axis interaction becomes stronger, but usually a broad transition region between cases c and b will follow. Finally the matrix element may become so strong that the fine-structure splitting is negligible and nearly pure Σ and Π states can be found. Due to a sudden transition of $V_{11}^{(2)}$ from large negative to large positive values one also gets a transition in Hund's case b–c–b. The re-orientation of the coupling in the region for case c again leads to an avoided crossing. Since the two b–c transitions are so close to each other this leads to one avoided crossing which can be easily localised by the condition

$$V_{11}^{(2)}(R_3) = 0.$$

The same also occurs at small internuclear distances. It is obvious that the neglect of the s–p interaction which led us to the equations above will not hold as well as in the cases above. However it will still be possible to determine the crossing radius R_2 by

$$V_{11}^{(2)}(R_2) = 0.$$

Until now discussing the couplings among the excited states we have only used the comparison between the orbit–axis and the spin–orbit interaction. For the coupling with the ground state we have to consider another mechanism. The coupling occurs high in the repulsive part of the potentials and we may neglect the spin–orbit interaction there. From the original energy matrix we obtain a 2 × 2 system connecting two Σ states one with the p and one with the s state as asymptotes (Baylis 1969a,b). The difference between these two states depends on various multipole moments but in the region in which we are interested, all of these are monotonic. The matrix element for the s–p interaction $V_{01}^{(1)}$, however, has a zero there. This leads to a minimum in the difference since the matrix element appears squared in the difference.

Table 2. Crossing radii and average energies in these radii (zeros of $V_{01}^{(1)}$, $V_{11}^{(2)}$ and $V_{11}^{(2)} - \frac{5}{3}E$).

System	R_1 (au)	$E_1^{(1)}$ (kK)	$E_1^{(2)}$ (kK)	R_2 (au)	E_2 (kK)	R_3 (au)	E_3 (kK)	R_4 (au)	E_4 (kK)
Na–Hg	— (3·70)	—	—	— (4·40)	—	11·350 (11·35)	16·72	19·65 (19·90)	16·95
K–Hg	4·580 (4·45)	27·39	29·62	4·770 (5·05)	31·53	11·950 (11·85)	12·79	17·90 (17·85)	12·98
Rb–Hg	4·845 (4·70)	26·95	29·29	5·105 (5·30)	29·00	12·00 (12·10)	12·51	15·50 —	12·62
Cs–Hg	5·200 (5·15)	25·51	27·83	5·57 (5·75)	25·14	11·60 (12·30)	11·35	16·20 —	11·44

The position of this zero will be given by the same considerations that have been discussed above with $V_{11}^{(2)}$. A difference will be that it is found at smaller internuclear distances since the less extended s function is involved. Thus finally we obtain for R_1:

$$V_{01}^{(1)}(R_1) = 0.$$

For practical purposes with these relations a simple and rapid method for the determination of the position of the avoided crossings is visible. Only a few and comparably simple radial integrals have to be evaluated to obtain a survey of the crossings. In the following section we will consider the reliability of these estimates.

It has been mentioned above that the systems considered here can be divided into two groups, Na, K and Rb, Cs, with respect to their fine-structure splitting. Despite their differences they have in common the general behaviour discussed above with the four avoided crossings which are shown in figure 4. These crossings, characterised by their radii and the average energy in these radii, are given in table 2. Besides the values obtained directly from the calculation we have given the values which are obtained from the estimates discussed above. The average deviation between the estimated and the true values in the table is 2·5% with the individual deviations ranging from 0 to 6%. In the light of the simplicity of the approximations these limits seem to be satisfactory. The missing entries in the table for the radii R_1 and R_2 for Na are due to a breakdown of the calculation in these cases, R_4 for Rb and Cs is missing because the equation for R_4 has no solution.

From the discussion of the position of the zeros of the matrix elements $V_{11}^{(2)}$ and $V_{01}^{(1)}$ one would expect the crossing radii R_1, R_2 and R_3 to be proportional to $\langle r^2 \rangle^{1/2}$. This relationship is fulfilled to a large extent as can be seen from figure 5. For R_1 and R_2 estimated and calculated radii can be approximated by a linear relationship with $\langle r^2 \rangle^{1/2}$. For R_3 this holds up to Rb and it is violated seriously by Cs. For this system the transition region is considerably broadened, due to the large fine-structure splitting, so that a clear recoupling of the angular momenta does not coincide with the zero of the respective matrix element.

The radii R_1, R_2 and R_3 increase for the heavier alkali atoms, while R_4 decreases. The reason for this decrease is that the increasing orbit–axis interaction competes with the fine-structure splitting. Our approximation properly reflects this decrease for Na and K. For Rb and Cs the approximation fails again since the fine-structure splitting dominates the complete outer region.
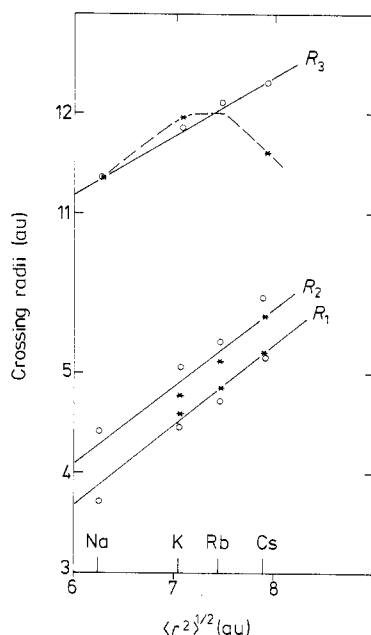
Figure 5. Relation of crossing radii with $\langle r^2 \rangle^{1/2}$. O, approximation; *, exact calculation.

3. Comparison of calculation and experimental results

The test of these calculated potentials by experiments has to probe two distinct areas. Firstly we have to investigate the basic assumptions in our model and only if this investigation yields positive results can we determine the potential matrix quantitatively in a second step.

Qualitative contributions to checking our model will be taken from the measurement of double-differential cross sections at 100 eV (Schädlich 1977) and from the measurement of integral cross sections at 500 eV (Moritz 1977). Quantitative comparisons will be made with the differential cross section for the ground state (Buck *et al* 1972, Hoppe 1977), the measured threshold for the excitation of the p state for K and Rb (Larsen and Herschbach 1977) and the ratio of the $j = \frac{3}{2}$ and $j = \frac{1}{2}$ excitation (Moritz 1977).

The qualitative comparisons refer to the basic assumptions of this model. One question is whether the Hg atom in this interaction can be represented by a polarisable density of electrons neglecting possible excitations. Thus we have to investigate the one-electron approximation. A second similar question is whether the four basis functions used in this calculation are sufficient. A necessary condition for these approximations to hold is that the excitation cross sections for the respective states are small compared with the ones taken into account here.

Indeed this relationship holds well as has been demonstrated in the state-specific experiments of our group in Göttingen. In the double-differential cross section experiments the excitation of the p states is found to be dominant in that all the remaining channels—higher states of the alkali and excitations of mercury—are excited with less than 1% probability (Schädlich 1977). In a more sensitive experiment the optical analysis of the spectra of the collisional excitation shows that the decays emitting radiation between 3000 Å and 8000 Å are less than 0·1% for K and Rb (Moritz 1977).
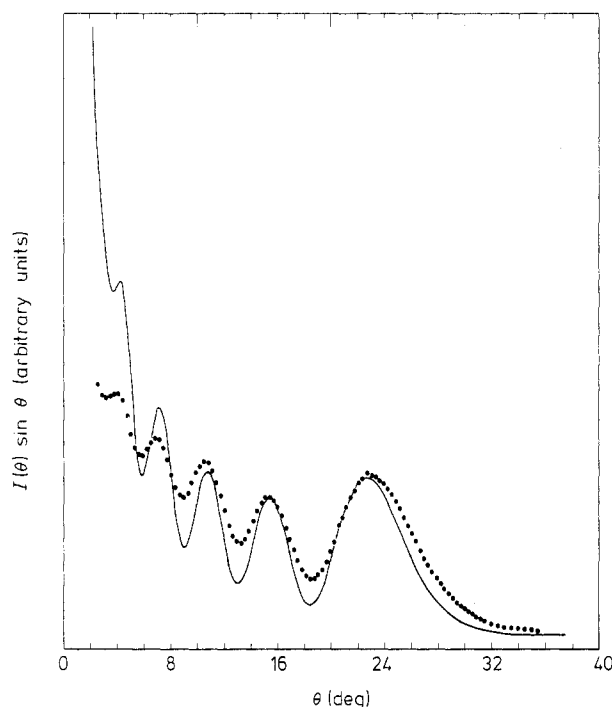
Figure 6. Differential cross section for the Na–Hg ground state interaction (from Hoppe 1977).

Since these results have been observed at high collision energies between 100 eV and 500 eV they hold *a fortiori* at the low energies that are relevant for the following quantitative comparisons.

The quantitative comparison with respect to the ground state has been discussed with the results of the calculations above (§2.2.2). To give an impression of the agreement between the measured cross sections and the theoretical ones we show the results in figure 6 (Hoppe 1977). The full curve represents the calculated WKB cross sections with the potential of our calculation. The dots are the experimental data.

The positions of the rainbow extrema are seen to match over a large range of angles. This reflects the agreement of experimental and calculated potentials displayed in figures 1 and 2 over a broad range of internuclear distances.

Finally we come to a first quantitative comparison with inelastic cross sections. The excitation cross sections for the ^{2}P states of K and Rb interacting with Hg have been measured recently with great resolution (Larsen and Herschbach 1977) and the results for the threshold energies are summarised in table 3.

The results agree within 2·5 kK which seems satisfactory especially in the light of the uncertainty of the threshold measurements, and the fact that in this case the calculated potentials at small internuclear distances are involved.

A second check against inelastic cross sections can be made with the energy dependence of the ratio of cross sections for the ^{2}P$_{3/2}$ and the ^{2}P$_{1/2}$ excitation for K–Hg (Moritz 1977). This ratio shows oscillations, which can be characterised by a parameter $\tau(b_0)$, which is equal to the phase difference for the two channels involved at its stationary point. Thus it is related to the integral over the difference between

Table 3.

	E_{exp} (kK)	E_{calc} (kK)
K–Hg	26	28·5
Rb–Hg	30	28·1

the respective potentials (Olson 1970). The comparison is given in table 4. Again the difference of 13% seems acceptable.

Table 4.

	$\tau(b_0)_{\text{exp}}$ (kK au)	$\tau(b_0)_{\text{calc}}$ (kK au)
K–Hg	86·5	74·9

4. Summary

Surveying the experimental and the calculated data for the alkali–mercury interaction one finds up to now no objections to the model calculation presented. Specifically the ground state interaction is reproduced quite well and the results from collisional excitation experiments are in reasonable agreement with the calculated results. These results have been obtained in a calculation, where the mercury target is visualised as a polarisable electron density for which no excited states have been taken into account in the basis functions of the expansion. The basis functions for the alkali states have been restricted to the ground state and the first P states. Both assumptions can be demonstrated to be reasonable in the light of collisional excitation experiments.

The main results of the potentials are the existence of four avoided crossings between the $m_j = \frac{1}{2}$ states, corresponding to radial couplings between these states. At small internuclear distances, with a threshold above the asymptote of the P state, the ground state couples with the excited states and the excited states with each other. Two further coupling regions connecting the excited states follow at medium and large internuclear distances. For these interactions the transitions between Hund's cases b and c are responsible. These can be expressed in terms of specific multipole moments of the expansion of the potential, by which a simple method for the determination of the crossing radii is developed. The comparison of the results of this approximation with the full calculation shows agreement within 6%.

In addition to the specific application to the systems investigated here, the pseudopotential calculations can be seen in a new aspect, namely as a convenient tool for interpreting experimental results. The advantages of this method are the fact that the interpretation is more remote from phenomenological assumptions than conventional (trial and error or inversion) methods. This is due to the fact that the model is shifted to a stage of the calculation where more physical parameters are to be described, namely the electronic interaction. One aspect of this is that parts of the total problem have been separated off and are treated in a well known fashion (e.g. the eigenfunctions for the various alkali metals). A consequence of this organisation of the problem is that the potentials for the excited states are calculated simultaneously with the ones for the ground state. The most important aspect, however,

is that in this approach a uniform representation of a class of collision systems can be given. Thus we describe the interaction of Na, K, Rb and Cs with Hg by two parameters in the pseudopotential which are constant for all these systems.

We are well aware of the limitations of the present calculations. Specifically we expect the limitation in number and accuracy of our basis, the approximation of an R-independent spin–orbit interaction and the neglect of the quadrupole polarisability to require improvements. However the order and the magnitude of the respective corrections are not yet apparent since the *present* experimental data are compatible with these calculations. Therefore we will wait for experimental work on these systems for a critical review and improvement of the model presented.

Acknowledgments

Note added in proof. In the further course of our investigations we found an extreme sensitivity of the potentials for the excited states to the fit of the calculated data with respect to the ground state. Thus a variation in the ground-state fit for ϵ of 3% can result in a variation of 25% for the well depth of the excited states. Obviously this uncertainty can only be resolved with a reliable experimental determination of the respective potentials.

References

Bates D R and Damgaard A 1949 *Phil. Trans. R. Soc.* A **242** 101
Baylis W E 1969a *J. Chem. Phys.* **51** 2665
——1969b *JILA Report* No 100
Buck U, Kick M and Pauly H 1972 *J. Chem. Phys.* **56** 3391
Düren R 1976 *Chem. Phys. Lett.* **39** 481
——1977a *Report MPI für Strömungsforschung* No 7
——1977b *Report MPI für Strömungsforschung* No 12
Düren R, Hoppe H-O and Pauly H 1976 *Phys. Rev. Lett.* **37** 743
Gombás P 1967 *Pseudopotentiale* (New York: Springer-Verlag)
Hoppe H-O 1977 *Dissertation* Göttingen
Larsen R A and Herschbach D R 1977 to be published
Masnou-Seeuws F and McCarroll R 1974 *J. Phys B: Atom. Molec. Phys.* **7** 2230
Mies F H 1973 *Phys. Rev.* A **7** 942
Moritz G 1977 *Dissertation* Göttingen
Nikitin E E 1965 *J. Chem. Phys.* **43** 744
Olson R E 1970 *Phys. Rev.* A **2** 121
Pascale J and Vandeplanque J 1974 *J. Chem. Phys.* **60** 2278
Reid R H G 1973 *J. Phys. B: Atom. Molec. Phys.* **6** 2018
Schädlich E 1977 *Dissertation* Göttingen
Smith F T 1969 *Phys. Rev.* **179** 111
Strunck V 1977 *Diplom-Thesis* Göttingen
Wilson A D and Shimoni Y 1974 *J. Phys B: Atom. Molec. Phys.* **7** 1543
Wüsthoff P 1936 *Ann. Phys., Lpz.* **27** 312