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Decoupling approximations in the quantum mechanical treatment of P-state atom collisions

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Several decoupling schemes are considered, for the effective simplifications of the close coupling equations which arise in the treatment of atomic collisions involving fine structure. Calculations were performed for two models of ^2P atoms colliding at thermal energy with a ^1S species. From the comparison of exact and approximate results, the relative merits and limits of full or partial decoupling schemes were assessed. Possible improvements and extensions are suggested.

I. INTRODUCTION

Although the quantum mechanical close coupling equations for atomic collisions involving fine structure effects can be easily written down when the relevant interactions are supposed to be known, their numerical solution is in general very time consuming, in particular because, for realistic problems at thermal energies, several hundreds of partial waves have to be considered. The need of suitable approximations is particularly urgent when, as is the case of the analysis of experimental results, the interactions are known only in an approximate way, and so, in absence of reliable inversion procedures, one would like to repeat the calculations several times by varying parts of the interactions in a trial and error attempt of fitting the experimental data.

In this paper, a set of approximation schemes will be developed based on the analysis of angular momentum coupling cases presented in the previous paper.[1] An important body of work, actually begun before the advent of the quantum close coupling method, has been carried on as far as approximations to this problem are concerned, but has been limited within the semiclassical context.[2] While this work has achieved remarkable results for the explanation of bulk properties and has brought into evidence the basic physics underlying the mechanism of these processes, the recent progress in the molecular beam studies of collisions of P atoms appears to require the full quantum mechanical treatment.

We will consider, in the following section, some decoupling approximations within the quantum mechanical close coupling framework. In Sec. III, two models of ^2P atom–^1S atom collisions will be described. They have been solved by the numerical methods expounded in Sec. IV, both exactly and under the various decoupling approximations. The results will be presented and discussed in Sec. V, and conclusions will be given in Sec. VI.

II. DECOUPLING APPROXIMATIONS

A. Full decoupling

When we refer to the set of angular momentum coupling schemes developed in the previous paper,[1] and further take into account the quantum numbers which are considered to be good in each of the five cases, decoupling approximations can be found by imposing conservation of some of these quantum numbers at all internuclear distances: This amounts to assuming the neglect of a part of the interactions that appear in the Hamiltonian.

As we have seen, the neglect of anisotropy in the electrostatic interaction leads to a full decoupling of the equations, since a representation can be found where both the centrifugal and spin–orbit terms of the Hamiltonian can be simultaneously diagonalized. This is evidently achieved neglecting the v_2 terms in the case (e) representation,[1] and amounts therefore to the trivial decoupling of the internal angular momenta of the atom from that of relative motion: It is expected to occur for any collision at sufficiently large interatomic distances or, even for moderate distances, at sufficiently large total angular momenta J.

To assume this decoupling situation requires trivially the solution of a set of one channel problems and leads to a diagonal S matrix, with elements $S^J_{j\bar{\epsilon},jl}$. Although evidently there is no use in considering this decoupling when inelastic effects are important, nevertheless we will find in the following that the application of this approximation for elastic problems is very useful in the drastic reduction of computing times, and therefore we will devote part of our attention to the effective determination of the minimum J above which, for a given energy and interaction, this approximation can be safely applied.

The opposite case with respect to this *atomic elastic* situation, where both j and l are conserved, arises when what we may term as *molecular elastic* decoupling occurs. This is the case when the electrostatic anisotropy is so large that both fine structure effects and the coupling due to the centrifugal interactions can be neglected. Formally, this amounts to assuming that both the spin–orbit splitting term and the centrifugal term are multiples of the unit matrix:

$$\mathcal{E} = \bar{\epsilon}\,1 \ , \tag{2.1}$$

$$\mathbf{l}^2 = \bar{l}(\bar{l}+1)\,1 \ . \tag{2.2}$$

Although there is some arbitrariness in the choice of $\bar{\epsilon}$ and $\bar{l}$ which appear in these equations, an obvious prescription for $\bar{\epsilon}$ in this problem is to take it as the "center of gravity" of the multiplet. As far as the mean orbital angular momentum is concerned, the simplest choice

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that we make in the following applications is to take it as equal to the total angular momentum J. However, it can be easily shown that this arbitrariness does not affect in a sensible way the final results. As a matter of fact, this approximation, which follows from Eqs. (2.1) and (2.2), is immediately recognized to be the analog to a popular approximation in the theory of rotational excitation,[3] where it is commonly referred to as the "infinite order sudden approximation" or the fixed spherical rotor model.

The result of assumptions (2.1) and (2.2) leads to complete decoupling of the multichannel equation (I-2.1) when they are written down both in the case (a) and case (c) representations.[1] One is then left to solve at a given energy a single channel problem for each Λ and J values. This will yield S matrix elements of unit modulus $S^J_\Lambda = \exp(2i\eta^J_\Lambda)$, from which the space-fixed S matrix can be constructed by a unitary orthogonal transformation, chosen at will as the (a)→(c) or (b)→(e) routes of Fig. 1 of the first paper:

$$\mathbf{S} = \mathbf{G}\exp(2i\boldsymbol{\eta})\,\mathbf{G}^{-1}\,, \tag{2.3}$$

where the G-matrix elements are those defined in Eqs. (I-3.1), (I-3.3), (I-3.4), and (I-3.5).

Since in this approximation, as in the previous one, the S matrix is built up of much fewer independent parameters than those which would be necessary if the problem were solved exactly, a set of relations is imposed among its matrix elements, and consequently among the various cross sections which are derived from them. For example, the three off-diagonal elements for each parity for the $^2P + {}^1S$ problem can be shown to be related by

$$\left|S^{J+}_{(3/2),J-(1/2);(3/2),J+(3/2)}\right|^2 = \frac{2J-1}{4J+4}\left|S^{J+}_{(1/2),J-(1/2);(3/2),J+(3/2)}\right|^2 \tag{2.4}$$

$$\left|S^{J-}_{(3/2),J+(1/2);(3/2),J-(3/2)}\right|^2 = \frac{2J+3}{4J}\left|S^{J-}_{(1/2),J+(1/2);(3/2),J-(3/2)}\right|^2,$$

which follow from the assumption in Eq. (2.1), and by

$$\left|S^{J+}_{(1/2),J-(1/2);(3/2),J+(3/2)}\right|^2 = \frac{6J+9}{2J-1}\left|S^{J+}_{(1/2),J-(1/2);(3/2),J-(1/2)}\right|^2,$$

$$\left|S^{J-}_{(1/2),J+(1/2);(3/2),J-(3/2)}\right|^2 = \frac{6J-3}{2J+3}\left|S^{J-}_{(1/2),J+(1/2);(3/2),J+(1/2)}\right|^2, \tag{2.5}$$

which follow from the assumption in Eq. (2.2). Many other relationships can be found among matrix elements, by working out the explicit expressions given by Eq. (2.3).

This molecular elastic approximation has been applied for Li(^2P) and Na(^2P) collisions with He by Bottcher, Cravens, and Dalgarno,[4] who also give the explicit relationships between elastic phase shifts η^J_Λ and integral cross sections for the ^2P–^1S case. A study of the validity of this approximation for Li(^2P)–He collisions has been carried out by Reid.[5]

B. Partial decoupling

Partial decoupling approximations can be derived by making only one of the two assumptions given by Eqs. (2.1) and (2.2).

Consider first that one wants to retain fine structure effects. Then only Eq. (2.2) needs to be assumed and since this amounts to imposing that Ω is a good quantum number throughout the collision, the close coupling equations partially decouple both in the case (c) and in the case (a) representations. Furthermore, the difference between the two sets belonging to the two different parities disappears. For example, for ^2P collisions, one is left to solve, instead of two 3×3 problems, only a single channel equation and a two state problem. Explicitly, in the case (c) representation, the radial wavefunction matrix

$$\mathbf{u} = \{u^\Omega_{jj'}\} = \begin{pmatrix} u^{1/2}_{1/2\,1/2} & u^{1/2}_{3/2\,1/2} & 0 \\ u^{1/2}_{3/2\,1/2} & u^{1/2}_{3/2\,3/2} & 0 \\ 0 & 0 & u^{3/2}_{3/2\,3/2} \end{pmatrix} \tag{2.6}$$

is obtained by using in Eqs. (I-2.1) and (I-2.2) the interaction

$$\mathbf{U} = \begin{pmatrix} \epsilon_{1/2} & 0 & 0 \\ 0 & \epsilon_{3/2} & 0 \\ 0 & 0 & \epsilon_{3/2} \end{pmatrix} + \left[\frac{\hbar^2\bar{l}(\bar{l}+1)}{2\mu R^2} + v_0\right]\mathbf{1} + \frac{v_2}{5}\begin{pmatrix} 0 & 2^{1/2} & 0 \\ 2^{1/2} & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{2.7}$$

Equivalently, in the case (a) representation, the matrix is

$$\mathbf{u} = \{u^\Omega_{\Lambda\Lambda'}\} = \begin{pmatrix} u^{1/2}_{11} & u^{1/2}_{01} & 0 \\ u^{1/2}_{01} & u^{1/2}_{00} & 0 \\ 0 & 0 & u^{3/2}_{11} \end{pmatrix} \tag{2.8}$$

and the interaction is

$$\mathbf{U} = \frac{1}{3}\begin{pmatrix} \epsilon_{3/2}+2\epsilon_{1/2} & 2^{1/2}(\epsilon_{3/2}-\epsilon_{1/2}) & 0 \\ 2^{1/2}(\epsilon_{3/2}-\epsilon_{1/2}) & 2\epsilon_{3/2}+\epsilon_{1/2} & 0 \\ 0 & 0 & 3\epsilon_{3/2} \end{pmatrix} + \left[\frac{\hbar^2\bar{l}(\bar{l}+1)}{2\mu R^2} + v_0\right]\mathbf{1} + \frac{v_2}{5}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{2.9}$$

the connection between the two representations being given by Eq. (I-3.3).

The solution of either of these simplified sets will lead to S matrix elements in the $|j\Omega\rangle$ or $|\Lambda\Omega\rangle$ representations, which give back those in the $|jl\rangle$ representation by the proper unitary transformations.[1] However, since the specification of the outgoing boundary conditions for the

wave functions requires linear combinations of Bessel functions obtained by means of the same transformations, in practice it will be convenient to make the transformations directly on the radial wave function matrix at the sufficiently large value of interatomic distances which is chosen as the end of the integration process.

As in previous cases, this approximation reduces the number of independent parameters in the S matrix elements, although not as drastic as in previous cases. For example, of the two relationships given above between off-diagonal S matrix elements, only Eqs. (2.5) are now valid.

It is immediately obvious, from the above considerations, that this Ω-*conserving* approximation is identical to a very widely investigated approximation in the theory of rotational excitation,[3,6] which is known in that context under many names, such as the j_z conserving, or helicity conserving, or spherical rotor, or coupled states approximation. To our knowledge, it has never been considered or applied to the present problem within the quantum mechanical framework, although essentially equivalent formulations within the semiclassical framework have been given by many authors,[7] each one proposing different semiclassical approaches to the solution of the 2×2 problem.

The alternative device which is available to obtain an effective partial decoupling of the close coupling equations consists of retaining the centrifugal effects, but neglecting those due to spin–orbit coupling. This can be done by making only the assumption given by Eq. (2.1).

This assumption leads to partial decoupling when the close coupling equations are written in the case (d) or (b) representations, and can be termed as the K-*conserving* or spin decoupling approximation.[8] Explicitly, in the case (d) representation, the radial wave function matrix

$$\mathbf{u}=\{u^K_{ll'}\}=\begin{pmatrix} u^K_{KK} & 0 & 0 \\ 0 & u^K_{K-1,K-1} & u^K_{K-1,K+1} \\ 0 & u^K_{K-1,K+1} & u^K_{K+1,K+1} \end{pmatrix} \tag{2.10}$$

is obtained by using in Eqs. (2.1) and (2.2) of the previous paper the interaction

$$\mathbf{U}=[\bar{\epsilon}+v_0]\mathbf{1}+\frac{\hbar^2}{2\mu R^2}\begin{pmatrix} K(K+1) & 0 & 0 \\ 0 & K(K-1) & 0 \\ 0 & 0 & (K+1)(K+2) \end{pmatrix}+\frac{v_2}{(2K+1)}\begin{pmatrix} -2K-1 & 0 & 0 \\ 0 & K-1 & -3[K(K+1)]^{1/2} \\ 0 & -3[K(K+1)]^{1/2} & K+2 \end{pmatrix}. \tag{2.11}$$

The same approximation can also be worked out in the case (b) representation. The radial matrix is then found to be

$$\mathbf{u}=\{u^{K\epsilon}_{\Lambda\Lambda'}\}=\begin{pmatrix} u^{K+}_{11} & 0 & 0 \\ 0 & u^{K-}_{11} & u^{K-}_{10} \\ 0 & u^{K-}_{10} & u^{K-}_{00} \end{pmatrix} \tag{2.12}$$

and the interaction is

$$\mathbf{U}=[\bar{\epsilon}+v_0]\mathbf{1}+\frac{\hbar^2}{2\mu R^2}\begin{pmatrix} K(K+1) & 0 & 0 \\ 0 & K(K+1) & -2[K(K+1)]^{1/2} \\ 0 & -2[K(K+1)]^{1/2} & K(K+1)+2 \end{pmatrix}+\frac{v_2}{5}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \tag{2.13}$$

the connection between the two representations being given by Eq. (I-3.6).

The above formulas show that the simplifications due to decoupling are similar both in the Ω-conserving approximation and in the K-conserving approximation. Also, considerations similar to the previous ones can be repeated here as far as restrictions on the number of independent parameters in the S-matrix elements, and relationships between the latter and the cross sections, are concerned. For example, of the two relationships between off-diagonal S-matrix elements which hold for full molecular elastic decoupling, only Eqs. (2.4) are now valid. Actually, Eqs. (2.4) have already been derived by Reid,[5] who has discussed at length spin uncoupling for Li(^2P)–He collisions, without however solving the explicit forms of the equations. Finally, it has to be noted that the K-conserving equations are essentially the same that are obtained in the treatment of collisions of ^1P atoms with a ^1S particle, where K is equal to the total angular momentum J because $S=0$. This problem has been discussed briefly in the previous paper,[1] where equations were given which are actually the limiting forms of Eqs. (2.10)–(2.13) for large total angular momenta.

III. DESCRIPTION OF THE MODELS

In order to test the various approximations derived in the previous section, we have considered two typical

models of a ^2P atom colliding with a ^1S species. The main difference between the two models lies in the fine-structure splitting: Accordingly, we refer to them as the large or small fine-structure splitting models. Since the experimental situations we are mostly interested in are those involving collisions at thermal energies, most of the exact and approximate calculations we have carried out refer to a collision energy of 0.0734 eV, as measured from the center of gravity of the doublet.

In the first model, we took the fine-structure splitting of the ^2P atom equal to that of fluorine, namely, 404 $cm^{-1} = 0.0501$ eV, the ground state corresponding to $j = 3/2$. This choice for a model with relatively large spin–orbit interaction was dictated in part by the fact that both experimental[9] and theoretical[10,11] work has already been reported on F(^2P) collisions. Most interesting for the present purpose is the fact that the fine-structure splitting in fluorine appears to be a good limiting case for a large spin–orbit interaction situation: A larger one should lead to a trivial decoupling of the fine-structure components at thermal energies.

For simplicity, we took both v_0 and v_2, the isotropic and anisotropic parts of the interaction,[1] respectively, to be of the Lennard-Jones (12-6) type. Specifically, we assumed (in atomic units)

$$v_0 = 4.016\times10^6 R^{-12} - 73.64\, R^{-6}\ , \qquad (3.1)$$

$$v_2 = -7.117\times10^6 R^{-12} + 12.54\, R^{-6}\ . \qquad (3.2)$$

With these values of the parameters, this models roughly simulates the F–Xe interaction as deduced from spectroscopic[12] and scattering studies,[11] and used in accurate recent close coupling calculations.[10] Accordingly, the reduced mass for this model was taken to be that of the F–Xe couple.

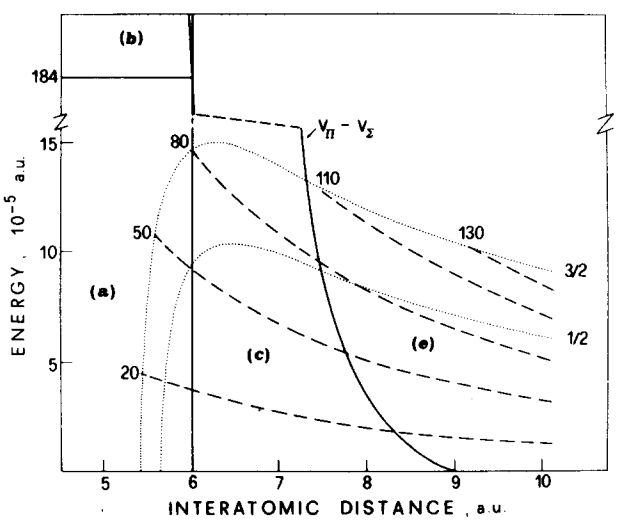

FIG. 1. Large fine-structure splitting model of Sec. III for $^2P-^1S$ collisions. The $v_\Pi - v_\Sigma$ curve is $-\frac{3}{5}v_2$ [Eq. (3.2)]: Its behavior with interatomic distance and the value of the fine-structure splitting at 184×10^{-3} a.u. divide the plane in five regions of dominance of Hund's cases, denoted by parenthesized lower-case letters (Ref. 1). [For case (d), which does not fit in this figure, see Fig. 2]. The dashed lines are centrifugal coupling terms of the indicated $\bar{l}$ values $2\bar{l}/\mu R^2$ (see Ref. 13). The two dotted lines connect the classical turning points as $\bar{l}$ varies, for scattering from the spherical part of the potential v_0 [Eq. (3.1)] at any energy of 0.0734 eV above the center of gravity of the atomic doublet, but measured as indicated either from the $j=\frac{1}{2}$ or $j=\frac{3}{2}$ state.

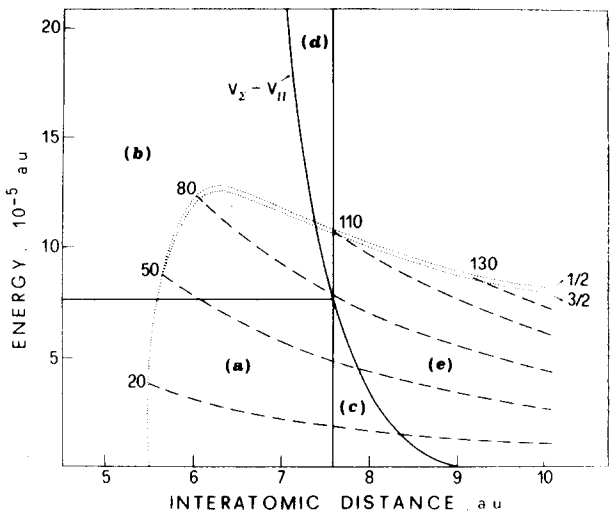

FIG. 2. Small fine-structure splitting model of Sec. III for $^2P-^1S$ collisions. The $v_\Sigma - v_\Pi$ curve is $-\frac{3}{5}v_2$ [Eq. (3.2)] and the fine-structure splitting at 7.8×10^{-5} a.u. is indicated. The other features are as in Fig. 1.

The second model we considered represents a case of fine-structure splitting substantially lower than the collision energy. We took 17.196 $cm^{-1} = 0.002132$ eV, which is the spin–orbit splitting in Na($3\,^2P$). Accordingly, the ground state for this case was taken for $j = 1/2$. Again, the reason for this choice has an experimental motivation: Scattering studies on sodium, laser excited to its $^2P_{3/2}$ component of the doublet, have recently been reported.[13] A smaller fine-structure splitting, such as for example that in Li($2\,^2P$) would lead to an effective spin uncoupling, as shown by Reid.[5]

As far as the electrostatic interaction is concerned, we took the same forms and parameters as in the previous model [Eqs. (3.1) and (3.2)]: However, in order to simulate in a qualitatively correct way the Na($3\,^2P$) interactions, the sign in v_2 was reversed. Finally, the reduced mass for this small spin–orbit interaction model was taken as that of the Na–Xe couple.

In order to have a first qualitative look at these models, we show in Figs. 1 and 2 the v_2 terms and the centrifugal coupling terms for different J values as a function of the internuclear distance. Also shown are the values of the spin–orbit splitting in each case. As is well known from semiclassical studies,[14] this type of plots is particularly useful in assessing the ranges of internuclear distances where a particular coupling scheme dominates. The ranges are also indicated in Figs. 1 and 2, where the centrifugal terms are drawn only down to the classical turning points for scattering from the spherical part of the potential v_0.

IV. NUMERICAL METHODS

For the two models described in the previous section, the exact close coupling equations in the $|jl\rangle$ or case (e)

representation[1] are a set of two 3×3 blocks of coupled differential equations of the second order. The program that we used for their solution is based on the log-derivative method proposed by Johnson.[15]

The criterion we have followed for the choice of the integration ranges and grids is essentially that adopted by Becker *et al.*[11]: This typically required from 5000 to 7000 integration steps for each J value, and the typical computing time for 125 J values was about 25 min on an IBM 370/158 computer.

Since we were concerned in this paper not with the immediate goal of reducing computing times, but rather with the assessment of the accuracy of the various decoupling approximations, we did not program them separately, but rather used the equations in the space-fixed formulation, introducing there the simplifications which arise from the approximations considered. In this way, we were able to compare the exact and approximate S-matrix elements in a very accurate way, regardless of biases in the programming.

A set of JWKB calculations of single channel equations which arose out of decoupling were also performed: Although these calculations required very little programming and negligible computing costs [they reduce to quadratures and were done on an HP 9825 A microcomputer], their accuracy was of the same order as that obtained with the close coupling program.

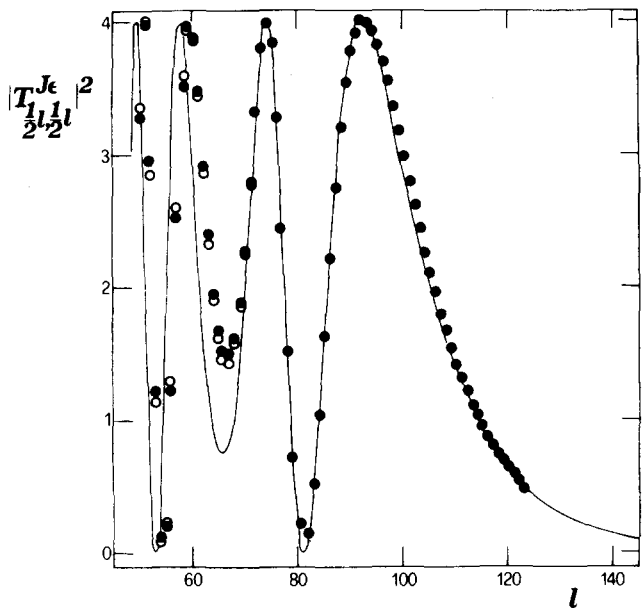

FIG. 3. Large fine-structure splitting model for ^2P–^1S collisions, at an energy of 0.0734 eV, as measured from the center of gravity of the atomic doublet. Absolute squares of diagonal T-matrix elements for $j=1/2$ are given as a function of the orbital angular momentum quantum number l. Exact results: black dots, $\epsilon=+1$, $l=J-(1/2)$; open dots, $\epsilon=-1$, $l=J+(1/2)$. The continuous curve connects single channel JWKB results for scattering from the v_0 potential at the same energy, measured from the $j=1/2$ atomic state.

V. RESULTS AND DISCUSSION

The numerical methods described in the previous section give the real and imaginary parts of the elements of the S matrix $S^{J\epsilon}_{jlj'l'}$ for a total angular momentum J and parity quantum number ϵ. The elements of the T matrix $T^{J\epsilon}_{jlj'l'}$ are generated by the relation

$$\mathbf{S}=\mathbf{1}-i\mathbf{T}\ , \tag{5.1}$$

and from them any cross section can be obtained. In particular, integral cross sections are calculated from the formulas

$$\sigma(j\to j')=\frac{\pi\hbar^2}{2\mu(2j+1)(E-\epsilon_j)}\sum_J(2J+1)\sum_{\epsilon ll'}|T^{J\epsilon}_{jlj'l'}|^2\ . \tag{5.2}$$

Since for the two models in Sec. III we are not interested in the cross sections *per se*, but rather on the reliability of approximations as compared with "exact" calculations, we limit our presentation to $|T^{J\epsilon}_{jlj'l'}|^2$ matrix elements. It is convenient to consider first the results of both exact and approximate calculations for those large J values, which are most important for elastic cross sections, and later the behavior at small and moderate J values, of interest for inelastic effects.

A. Large J values and elastic cross sections

With reference to Figs. 1 and 2, it is immediately seen that, for both models, at J values larger than about 100, the classical turning points limit the range of interatomic distances which are probed by the collisions, within a regime of weak electrostatic interactions, typical of a case (e) description. Since, in order to obtain converged values for the elastic cross sections, it is necessary to extend the summations in Eq. (5.2) to J values larger than 500 even at the thermal energies considered here, it is obvious that it is very important to determine the J values at which the conditions for the full atomic decoupling of Sec. II A are fulfilled.

In Figs. 3–6, the absolute squares of the diagonal elements of the T matrix are presented for the two models as a function of the orbital angular momentum l. It is seen that, for both models, they tend to coincide at the same value, for any given j and l, as the latter increases, any distinction due to parity and to any dependence upon the total angular momentum J being progressively lost. As this happens, of course, the corresponding T-matrix elements tend to unit modulus, while the off-diagonal ones tend to vanish.

The curves drawn in the same Figs. 3–6 show the results of single channel JWKB calculations of T matrices for scattering from the v_0 potentials for collision energies measured from that of the appropriate j level. As can be seen, this elastic atomic approximation works extremely well under the conditions where both j and l are effectively conserved: Of course, that this would happen was not unexpected. What is interesting is that from an inspection of Figs. 1 and 2 it can be anticipated quantitatively where this decoupling occurs. Specifically, for the large spin–orbit model, Fig. 1 suggests and Figs. 3 and 4 confirm that it occurs for $J\gtrsim80$ for $j=1/2$, and for $J\gtrsim115$ for $j=3/2$. For the small spin–orbit model, Fig. 2 anticipates and Figs. 5 and 6 prove that the decoupling, for both $j=1/2$ and $j=3/2$, is effective for J values larger than $\simeq110$.

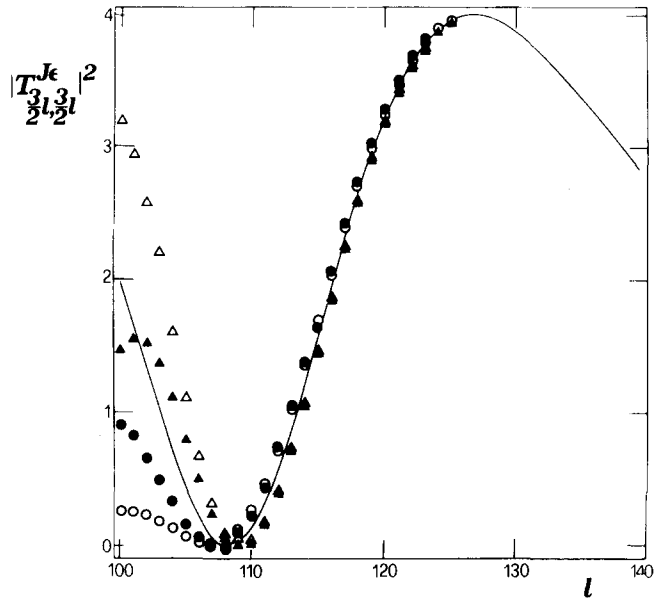

FIG. 4. Large fine-structure splitting model for $^2P-{}^1S$ collisions, at an energy of 0.0734 eV as measured from the center of gravity of the atomic doublet. Absolute squares of diagonal T-matrix elements for $j=3/2$ are given as a function of the orbital angular momentum quantum number l. Exact results: black dots, $\epsilon=+1$, $l=J-(1/2)$; open dots, $\epsilon=-1$, $l=J+(1/2)$; black triangles, $\epsilon=+1$, $l=J+(3/2)$; open triangles, $\epsilon=-1$, $l=J-(3/2)$. The continuous curve connects single channel JWKB results for scattering from the v_0 potential at the same energy, measured from the $j=3/2$ atomic state.

B. Small J values and inelastic cross sections

For J values smaller than about 100, as can be anticipated from Figs. 1 and 2, the conservation of j and l quantum numbers is no longer expected to hold, coupling schemes other than (e) become operative, and therefore inelastic effects become important.

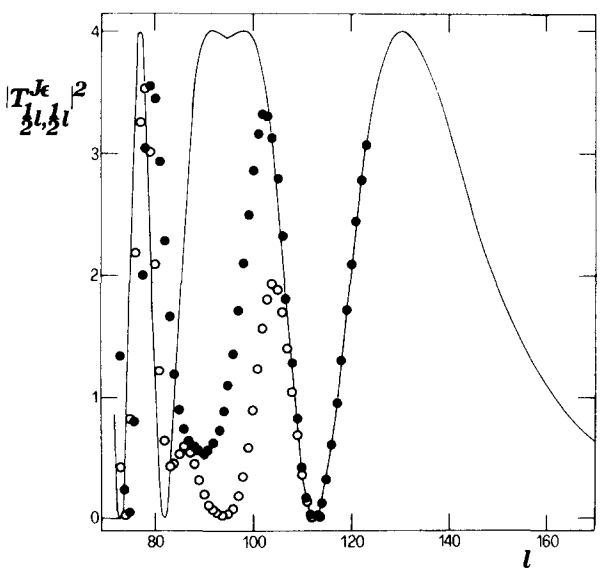

FIG. 5. Small fine-structure splitting model for $^2P-{}^1S$ collisions, at an energy of 0.0734 eV, as measured from the center of gravity of the atomic doublet. The meaning of the symbols and of the curve is as in Fig. 3.

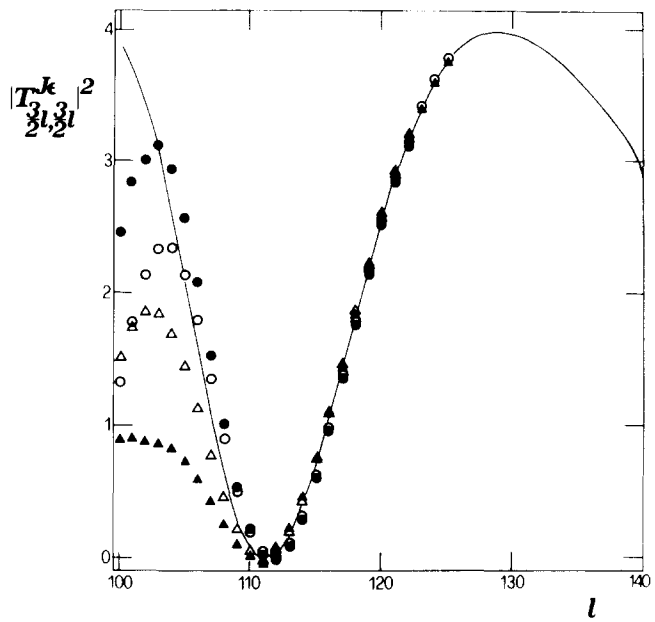

FIG. 6. Small fine-structure splitting model for $^2P-{}^1S$ collisions, at an energy of 0.0734 eV, as measured from the center of gravity of the atomic doublet. The meaning of the symbols and of the curve is as in Fig. 4.

An inspection of Figs. 1 and 2 shows that, for none of the two models, angular momenta can be found where K conservation, or spin uncoupling conditions were met. In fact, a comparison of exact results and the approximate ones in the K-conserving formulation showed that the latter gives very bad results. As a matter of fact, an inspection of the exact results has shown that Eqs. (2.4)–(2.7) are never satisfied for these models. *A fortiori*, no reliability is expected for the molecular elastic approximation of Sec. IIA, and this was demonstrated numerically by the poor results we obtained by using this approximation at this energy. Although we did not study in detail those conditions under which the K-conserving and the elastic approximations are reliable, we analyzed some sample calculation for the large spin–orbit situation and found that an order of magnitude increase in the energy was necessary to obtain that the conditions in Eqs. (2.4)–(2.7) were satisfied, and then only at rather small J values. This supports Reid's finding,[5] that K-conserving, or spin uncoupling conditions for most partial waves are met only for collision energies at least two orders of magnitude larger than the spin–orbit splitting.

As Fig. 7 shows, very good agreement was obtained between the exact results and those obtained in the Ω-conserving approximation for the large fine-structure splitting model for J values less than $\simeq 50$. As a consequence, a nearly exact cross section for the fine-structure transition was obtained in this case, using this approximation. This result can be explained by reference to Fig. 1, which shows that for J up to $\simeq 50$, the collisions take place under conditions best described under case (a) and (c) coupling schemes, both involving Ω as a quantum number for the expansion basis.

Of course, the approximation deteriorates as J in-

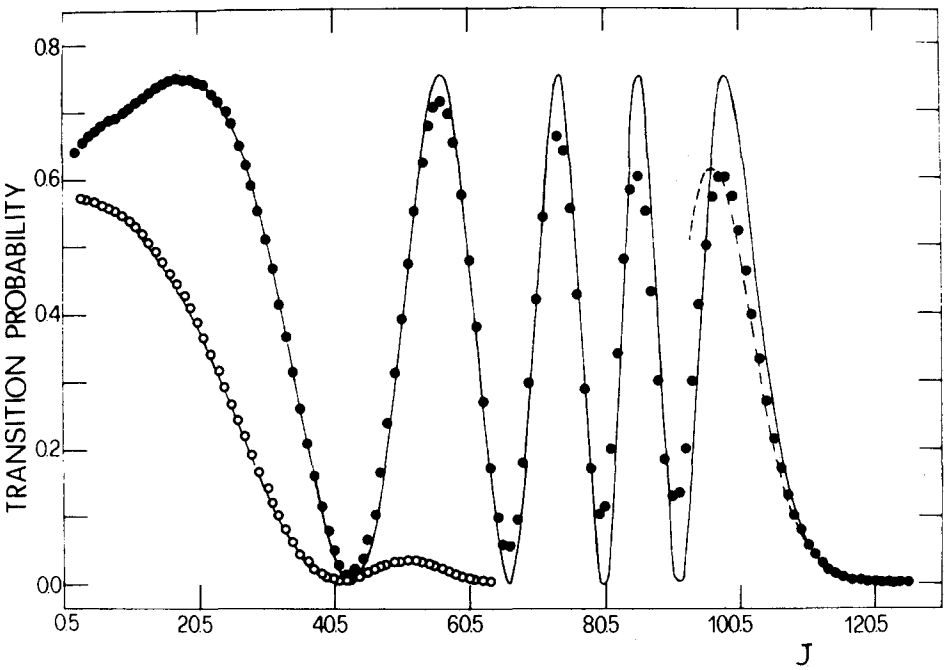

FIG. 7. Large fine-structure splitting model for $^2P - {}^1S$ collisions, at an energy of 0.0734 eV, as measured from the center of gravity of the atomic doublet. Weighted sums of absolute squares of off-diagonal T-matrix elements, as a function of the total angular momentum quantum number J. Exact results: black dots: $(1/4)\sum_{\epsilon ll'} |T^{J\epsilon}_{(3/2)l/(3/2)l'}|^2$, for $l \neq l'$ contributing to transitions among magnetic sublevels within the $j = 3/2$ atomic state); open dots: $(1/2)\sum_{\epsilon ll'} |T^{J\epsilon}_{(1/2)l,(3/2)l'}|^2$ multiplied by 10^2 [the sum in Eq. (5.2) for the transitions $j = \frac{1}{2} \rightarrow j' = \frac{3}{2}$, between the fine-structure components of the ^2P atom]. The continuous curves connect the results obtained within the Ω-conserving approximation, while the broken curve connects the results of a j-conserving assumption.

creases. However, for a limited range of J values, from $\simeq 100$ to the onset of j and l decoupling, conditions are met where j is already a good quantum number, even though some l mixing still takes place. Therefore, we ran calculations in this range by assuming j conservation, i.e., by neglecting matrix elements connecting channels with $j \neq j'$; these results are also shown in Fig. 7.

As far as the model with small fine-structure separation is concerned, it was found that none of the decoupling schemes considered gave satisfactory approximations to the exact results for the off-diagonal matrix elements, and therefore we omit the presentation of the results for this case. Again, reference to Fig. 2 shows that apart from the full decoupling which takes place at large J values, and which has been considered previously, collisions involving those J values which determine inelastic effects take place through a sequence of various coupling schemes, and so no single quantum number can be considered as conserved for the whole collisions. This determines the failure of decoupling approximations for this model, as far as inelastic effects at this energy are concerned.

VI. CONCLUSIONS

The analysis developed in the preceding paper[1] on the angular momentum coupling schemes within the quantum mechanical framework, necessary for the description of fine-structure effects in low energy atomic collisions, has been used here to discuss the usefulness of full or partial decoupling approximations for these problems. The numerical examples treated in this paper have shown that situations can be found where simplifications along these lines can be effectively achieved.

For example, the Ω-conserving approximation gives essentially exact results for intramultiplet transitions when the fine-structure splitting is relatively large, but predicts correctly transitions among the magnetic sublevels only for small J values. Furthermore, as already known from Reid's studies,[5] we confirm that no reliable approximations of this kind can be found, when the fine-structure splitting is small but not negligible with respect to the collision energy.

On the other hand, approximations based on sudden changes of coupling schemes, such as those introduced within the semiclassical framework,[3] and used to predict in a simple way bulk properties, could be easily formulated within the quantum mechanical framework developed previously.[1] Improvements can also be formulated, based for example on combined JWKB-exponential approximation methods, in order to allow "smoother" transitions between Hund's cases. It remains to be seen whether the unavoidable complications, which arise in the programming of these approximations, will be compensated by an effective gain in computing times, without severe losses in the accuracy which can be obtained by the "brute force" solution of the close coupling equations.

However, a very useful compromise, which this work strongly supports, and which we are investigating for problems of larger dimensionality than the ones considered here, can be devised, especially for the time-consuming problem of computing elastic cross sections.

In Sec. VI, it was shown that J values can always be found, where effective j and l decoupling occurs, and the use of the simple JWKB single channel procedure is strongly recommended in this J range: For our examples, which are quite typical, this already reduced by a factor of 5 the computing times for elastic cross sections. Furthermore, even at small J values, as Figs. 1 and 2 show, the j and l decoupling occurs at interatomic distances close enough that it appears to be safe in practice to restrict the exact solution of the close coupling equations within a typically small R range, e.g., from a few wavelengths before the classical turning points to a few wavelengths inside the (e) region. The radial wave function matrix can be then connected, and propagated at larger R values, by JWKB single channel wave functions. This procedure should allow an order of magnitude saving in computing times, while still involving simplicity in programming and no loss in accuracy.

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