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Chemical Physics 349 (2008) 170–180

Chemical Physics

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Correlation of attack and recoil angles for the Li + HF reaction: An exact quantum mechanical study at low and high total angular momentum

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Received 28 November 2007; accepted 20 February 2008
Available online 26 February 2008

Abstract

The total angular momentum ($J = 1$, 10) S matrix elements of the Li + HF reaction have been calculated using a time independent method, and matrix transformed to the stereodirected and Gauss–Legendre discrete variable representations. This paper extends to higher partial waves the study on the stereodynamics of the Li + HF reaction performed at a total angular momentum $J = 0$. The work is focused on the orbital angular momentum (L) substates rather than on the projections K on the intermolecular axis and emphasis is given to a space-fixed rather than to a body fixed view of the collision process. A detailed comparison of stereodirected and discrete variable representations is also made.

Keywords: Stereodynamics; Stereodirected; DVR; Reaction; Li + HF; Probability

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1. Introduction

The state to state S matrix element is the most detailed piece of information obtainable from a scattering calculation (with "state" meaning both channel and partial wave).

By means of unitary transformations, the S matrix can be expressed in a multitude of different representations. The great majority of these provide no physical insight, and are therefore not used. For obvious reasons, the preferred representation of asymptotic states is the one where the particles are characterised by well defined rotational angular momentum and vibrational quantum numbers (j, v), as well as a definite relative translational energy (E_{tr}).

However, alternative representations can provide complementary pictures of the scattering event which can lead to an increased understanding of the mechanisms governing elementary molecular collision processes. The use of these alternative representations can be of help in elucidating the results of stereodynamic experiments [1,2].

The correlation between attack and recoil angles for the Li + HF reaction [3,4] has been analysed by Alvariño et al. [3] using the stereodirected representation (SDR) of Aquilanti et al. [5,6]. The stereodynamics of the Li + HF reaction has also attracted other theoretical work [7–10].

More recently, we have focused our attention on the DVR method developed by Light and coworkers [11–13]. Using this method, we have calculated reaction probabilities for specific attack and recoil angles using a Gauss–Legendre quadrature DVR representation for the angular localisation [14,15]. We have compared the results obtained this way with the corresponding SDR ones, illustrating important differences between the two methods.

In the present paper, a comparison between results obtained using the SDR method and those obtained using the DVR one for the Li + HF reaction at a total angular momentum $J = 1$ and $J = 10$ is considered. Our aim is to

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0301-0104/$ - see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.chemphys.2008.02.037

compare the predictions of the two methods as the energy of the collisional process increases (and higher total angular momenta come into play) not only to compare the relative accuracy of the two approaches, but also to understand the validity of those approximations which estimate higher J contributions to reaction cross sections by shifting in energy the $J = 0$ ones.

The S matrix elements needed for our study have been partly obtained from both time independent [16,17] and time-dependent calculations [18,19] previously published and already used to investigate angular correlation effects [10] and partly produced for the present paper. These S matrices have been transformed into both the SDR and the DVR representations which essentially constitute linear combinations of reactant and product rotational states. We have then calculated reaction probabilities in these alternative representations to work out information regarding the angular dependence of the reaction, and in particular the correlation between the attack and recoil angle of the triatomic system.

The organisation of the paper is as follows: in Section 2, the computational procedure is illustrated, along with the two angle-specific representations utilised. In Section 3, results are presented, a discussion is made in order to rationalise the observed trends and some conclusions are given.

2. Theory

The S matrix elements, as mentioned in Section 1, have been obtained through a time independent calculation on the $\mathrm{Li} + \mathrm{HF}(v, j) \rightarrow \mathrm{LiF}(v', j') + \mathrm{H}$ reaction (from now on, unprimed quantities refer to reactants whereas primed ones refer to products).

It is reminded that one of the advantages of time independent methods is the fact that one can obtain results (at a single total energy E) for all possible asymptotic channels with only one calculation. Here we briefly outline the theoretical aspects of our work, referring to our previous paper [15] for more details and caveats of the method.

2.1. S matrix transformation

Once the S matrix is obtained in this way, it is expressed in what was termed before the $v\,j$ representation. This can then be transformed to an alternative representation using the standard technique of matrix transformation by inserting two complete sets into the matrix element of the $\widehat{S}$ operator:

$$\langle v't'|\widehat{S}|vt\rangle = \sum_{j,j'} \langle v't'|v'j'\rangle \langle v'j'|\widehat{S}|vj\rangle \langle vj|vt\rangle \tag{1}$$

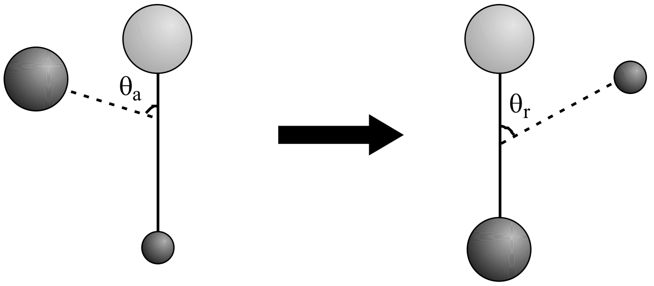

Fig. 1. Illustration of a 3-particle collision, along with the definition of attack and recoil angles as used in the text.

Here t denotes a generic quantum number. Normally it would be chosen in such a way that the states $|vt\rangle$ are, in the relevant Hilbert space, near minima of the uncertainties of observables of physical relevance. As a trivial example, $|vj\rangle$ states represent zero uncertainty in the rotational angular momentum. The situation, however, is more complicated when one considers continuous observables, such as angles. In order to derive information relevant to establishing correlations between attack and recoil angles, the $v\ t$ wavefunctions should be localised as much as possible around a restricted interval of angle values. This way, the transformed S matrix elements provide us with information regarding angular selectivity and specificity of the reaction under consideration. The angles mentioned here are termed as *attack* and *recoil* angles for the reactant and product arrangements respectively. The attack angle θ_a is defined (for a generic $\mathrm{A} + \mathrm{BC}$ system) as the angle formed by the interatomic vector of the reactant diatom (the BC vector) and the vector pointing from the centre of mass of the diatom towards the atom (the $\mathrm{A} - \mathrm{BC}$ vector) as shown in the left hand side scheme of Fig. 1. The recoil angle θ_r is defined as the angle formed by the interatomic vector of the product diatom and the vector pointing from the centre of mass of the product diatom towards the atom (see right hand side scheme of Fig. 1). Being essentially altitude angles, both θ_a and θ_r range between 0° and 180°.

Obviously, the vt representation is discrete in the same way the vj representation is, and some degree of angular delocalisation is always to be expected.

2.2. Remarks on angle localisation

The uncertainty principle between angle and angular momentum is a limit to the angular resolution that can be obtained. The more the angle is to be localised, the larger is the number of j states that have to be included in the set. Conversely, the fewer j states are included, the more diffuse the angle-localised wavefunction is going to be. In our angle-localised basis set, the maximum j (j_max) we are using must be included as an extra parameter, as the resulting angle-localised wavefunction will certainly depend on its value.

Another limit is imposed by energy conservation. If the total energy E of our reactant or product state is known and fixed, the number of diatomic j states we can coherently combine is obviously bounded up by energetic considerations. Hence, other things (such as moments of inertia of the relevant diatomic molecule) being equal, low total energy necessarily implies a low angular resolution.