TRANSLATIONAL ENERGY DISPOSAL IN MOLECULAR COLLISIONS: 
THE TRANSFER OF MOMENTUM CONSTRAINT

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A Franck-Condon type argument, which requires the least transfer of momentum to the nuclei during a collision is outlined and applied to the analysis of translational energy disposal and its dependence on the initial translational energy. Using the maximal entropy procedure of information theory we are able to proceed directly from the assumed (model) constraint to the product state distribution.

1. Introduction

The molecular (and ion) beam scattering technique provides the possibility of measuring the angular and recoil energy distribution of reaction products [1]. Similarly such results are the direct output of classical trajectory computations. It is therefore useful to develop a systematic procedure for the analysis of such data.

The second aim of this work is to demonstrate the use of information theory [2-4] and, in particular, the maximum entropy principle when coupled with models (or approximations) for the collision dynamics. Specifically, we use the (simplified picture of the) collision to identify a constraint on the dynamics and then proceed to determine the least-biased distribution which is consistent with this constraint. In this way one can compare the model directly with the experimental (or trajectory-computed) results without bringing in any additional approximations.

To analyze the translational energy distribution we have invoked the transfer of momentum constraint. The physical origins and significance of the constraint is considered in section 2. Section 3 shows how the same constraint appears in the Born approximation for the collision dynamics. Having determined a constraint we show, in section 4, how information theory can be brought in to generate the products recoil energy distribution. The functional form we obtain is

$$P(E_T) = P^0(E_T') \exp \{-\lambda_T [(E_T')^{1/2} - e^{1/2}]^2 - \lambda_0 \}. \quad (1)$$

Here $E_T'$ is the products (c.m.) translational energy and $P^0(E_T')$ is the prior distribution [2-4]. $\lambda_T$ and $\lambda_0$ are information-theoretic Lagrange multipliers and $e$ is a parameter of the model. At a well-defined total energy $E$ and in the RRHO approximation [3,4]

$$P^0(E_T') = (15/4)(E_T')^{1/2}(E - E_T')/E^{5/2}. \quad (2)$$

$\lambda_0$ is a constant that ensures that $P(E_T')$ is normalized. $\lambda_T$ and $e$ are usually best determined by fitting (1) to the observed distribution. There is however a distinction between these two parameters. $\lambda_T$ appears in the derivation as a Lagrange multiplier chosen so as to render $P(E_T')$ consistent with the dynamic constraint while $e$ is a theoretical parameter, which is essentially a measure of the momentum of the ejected atom. In
Fig. 1. Surprising analysis of the experimental \( P(E_T) \) distribution \([5]\) for \( \text{Rb}^+\text{CH}_3\text{I} \) at \( E_T = 4.46 \text{ kcal/mole} \). The parameter \( e \) was determined by a fit of (1) to the observed distribution. The entropy of the fitted functional form relative to the raw experimental data is 0.001 eu, indicating a very good fit. 80\% of the distribution is confined within the range \([ (E_T)^{1/2} - e^{1/2}]^2 < 1 \text{ kcal/mole} \); \( e = 19.6 \text{ kcal/mole} \), \( \lambda_T = 0.88 \text{ (kcal/mole)}^{-1} \). The straight line is the theoretical fit.

![Graph showing the distribution](image)

Also the dependence on initial conditions. A similar analysis was carried out for non-reactive (but inelastic) trajectory results for the \( \text{Cl} + \text{HI} \) reaction, where \( e^{1/2} = E_T^{1/2} \) provides a satisfactory representation. We thus conclude that the momentum transfer model, which has received considerable attention in the past (cf. sections 2 and 3) is able to account both qualitatively and quantitatively (by a suitable choice for \( e \)) for the observed recoil energy distribution.

2. The momentum constraint

The Franck–Condon principle is essentially the
principle of minimal momentum transfer to the nuclei during the rapid electronic transition. It has long been suggested that a similar principle should operate for direct molecular collisions [9-14]. The original statements were either derived from the Born approximation [9, 13-16] or reasoned on physical grounds. Subsequently, the examination of experimental and trajectory generated distributions led to the observation that for a "repulsive" release of the reaction exothermicity an impulse is imparted to the departing atom [17] thereby leading to the, so called, DIPR model [17, 18] and, in general, to the class of "retreat coordinate release" [19-21] and "photodissociation" [22] (or DIPR DIP) models. In addition, it was recognised [23-27] that elastic collisions, between pairs of atoms, during the overall reactive encounter would modify the momenta of the nuclei.

The first Born approximation is not expected to provide an accurate description of all aspects of the collision. Similarly, the physically motivated models often need the injection of additional assumptions in order to provide a dynamical theory that can be tested against experiment. The question naturally arises as to how one can retain the essential physical concept of the reaction dynamics, discard the peripheral assumptions and yet derive results that can be compared with experiment. In this note we demonstrate the application of information theory to this problem. We show how one can go directly from an assumed momentum transfer to a product recoil energy distribution.

3. The Born approximation

As an illustration, we consider in some detail the use of the Born approximation as a source of a dynamical constraint. Let \( k_i \) and \( k_f \) be the initial and final relative momenta \( (E_T = \hbar^2 k_i^2/2\mu_i, \mu_i = m_A(m_B+m_C)/(m_A+m_B+m_C) \) and similarly for the final state). It is convenient to define the two "momentum transfers" [13]

\[
Q_C = -k_f + \gamma_i k_i = -k_f + k_C, \\
Q_A = -k_i + \gamma_f k_f = -k_i + k_A, \tag{5}
\]

where \( \gamma_f = m_A/(m_A+m_B), \gamma_i = m_C/(m_B+m_C) \) and note that

\[
Q = E_T - E_T = (\hbar^2 q_C^2/2\mu_{BC}) - (\hbar^2 q_A^2/2\mu_{AB}), \tag{6}
\]

with \( \mu_{BC} = m_B m_C/(m_B+m_C) \). The momentum transfer \( q_C \) is the change in the momentum of the ejected atom \( \varepsilon \) during an \( A+BC \to AB+C \) collision.

The precise form of the Born amplitude depends on the details of the potential energy surface. For the exchange of a light atom between two heavier ones one can argue on physical grounds [13] and prove [28] that the leading term, in the first order Born expression will be determined by the \( B-C \) interaction (since the \( A-C \) interaction will be essentially along the internuclear distance). This term can be readily evaluated [13-16]. Taking (for simplicity) a collinear collision it yields (up to a weakly energy dependent factor)

\[
P_C(E_T \to E_f) = p_C^0(E_T) p_C^0(E_f) |g_{AB}(q_A)|^2 |g_{BC}(q_C)|^2, \tag{7}
\]

Here \( p_C^0(E_f) \) is the prior distribution for the collinear case, \( p_C^0(E_f) = (2\pi)^{-1/2} \). If \( g_{BC}(q_C) \) is the form factor, i.e., the wavefunction for the BC vibrational motion in momentum space, and similarly for \( g_{AB}(q_A) \).

For a harmonic oscillator in the \( n \)th level and putting \( Z_C = 2(\hbar^2 q_C^2/2\mu_{BC})/\hbar \omega_{BC} \),

\[
|g_{BC}(q_C)|^2 = N_n H_n^2(Z_C^2) \exp(-Z_C) \tag{8}
\]

Here \( N_n \) is a normalization factor and \( H_n \) is the Hermite polynomial.

The wavefunction in momentum space (the form factor) is peaked near the classical equivalence point, i.e., \( Z_C \) \( \text{m.p.} = 2n \), (or \( (\hbar^2 q_C^2/2\mu_{BC}) \text{m.p.} = E_n = n! \omega_{BC} \)). In precisely the same way that the wavefunction in coordinate space is concentrated about its classical turning point. The distribution of values of \( q_C \) in the collision should be centered about the most probable value,

\[
(\hbar^2 q_C^2/2\mu_{BC}) = \langle Z_C \rangle (\hbar \omega_{BC}/2), \tag{9}
\]

where the brackets denote an average over the distribution of products. Similar considerations apply to \( g_{AB}(q_A) \).
1. Information theoretic considerations

We need to determine the products $E'_T$ distribution subject to the constraint that $\langle Z_C/2 \rangle$

$$\langle Z_C/2 \rangle = \langle (\hbar^2 q_C^2/2\mu_{BC})/\hbar \omega_{BC} \rangle$$

$= \langle [(E'_T)^{1/2} - \cos \beta E'_T^{1/2}]^2 \rangle/\hbar \omega_{BC} \sin^2 \beta$, \hspace{1cm} (10)

is known. The information theoretic solution [2–4] is uniquely specified by the condition that the distribution, apart from reproducing the known value of $\langle Z_C \rangle$, has the minimal possible information content. This procedure gives

$$P_C(E'_T) = P_C^0(E'_T) \exp (-\lambda Z_C - \lambda_0)$$

$$= P_C^0(E'_T) \exp \{-\lambda_T [(E'_T)^{1/2} - e^{1/2}]^2 - \lambda_0\}, \hspace{1cm} (11)$$

with $e = E_T \cos^2 \beta$. Here $\lambda$ (or $\lambda_T$) is determined by the condition that $\langle Z_C \rangle$ has its specified value and $\lambda_0$ ensures that $P(E'_T)$ is normalized.

The simplest route to the three-dimensional distribution is to argue [29] that $P(E'_T)/P^0(E'_T)$ should be approximately the same for collinear and three-dimensional collisions (barring the obvious exceptions). The trajectory results for the Cl+HI reaction, fig. 3, validate this expectation. Hence (11) essentially implies (1).

The information-theoretic distribution (11) is consistent with the constraint of minimal momentum transfer and is, otherwise, the least biased\*. The success of (1) in accounting for (certainly the overall) features of the observed (or computed) recoil energy distribution verifies therefore that the principle of minimal momentum transfer does govern the translational energy distribution\**.

A direct route to the three-dimensional distribution is to regard $q_C$ in (10) as the vector momentum transfer and determine the distribution accordingly. As is evident from fig. 1, up to small correction factors this route also leads to† (1).

5. Repulsive energy release

In section 3 we were concerned with a spectator atom $C$ whose momentum, $k_C = \gamma_i \hat{k}_i$ is just its share ($\gamma_i = m_C/(m_B + m_C)$) of the incident momentum. Since $C$ need not sit idly, all one can say in complete generality is that $e = h^2 k_C^2/2\mu_f$ where $k_C$ is the momentum of the $C$ atom as determined by the collision dynamics. The procedure is then to adopt a model of the dynamics, compute $k_C$ and hence $\epsilon$ and compare the resulting distribution, (1), with the experimental or detailed-computational results. Two particular cases deserve however a special mention\††. The first is reaction on a repulsive (or late downhill) surface. A simplistic view (e.g., refs. [1,31]) of such reactions imme-

\* There is no other distribution which is consistent with the constraint and requires fewer additional dynamical assumptions in its derivation. In fact, (11) requires no additional assumption beyond the constraint.

\** In addition, this distribution is consistent with the observed vibrational energy disposal as measured by chemiluminescence or chemical laser methods [1]. The dynamic constraint which has been invoked for these systems [30] can be related to the constraint used here.

† Except, of course, that the second route also provides a constraint on the direction of $q_C$ and hence provides the joint recoil energy-angular distribution which is then integrated over all angles.

†† These two cases, discussed here from a physical point of view can be derived within the framework of collision theory.
diately suggests that the late release of the exoergicity, past the initial A–BC encounter, ejects the atom C with high translational energy. Such repulsive release is also at the heart of the photodissociation mode [22]. The physical picture corresponds to taking $k_C = \gamma k_1 + I$ where $I$ is the impulse imparted during the repulsive release of the energy $R, R = h^2 l^2 / 2 \mu_{BC}$. Now $e^{1/2} = \cos \beta E_T^{1/2} + \sin \beta R^{1/2}$. While this result nicely accounts for the qualitative dependence of $e$ on $E_T$ for most processes (and quantitatively for Cl+HI) it often (e.g., H+XY or M+CH$_3$I) fails to correctly predict the slope of $e^{1/2}$ versus $E_T^{1/2}$. Its most serious flaw is that it errs on qualitative trends (e.g., the effect of replacing $M = K$ by $M = \text{Rb}$ or $H+\text{Cl}_2$ versus $D+\text{Cl}_2$).

This introduces the need for the second modification. The momentum of C need not be just its incident momentum plus any repulsively released exoergicity. It can also change due to A–C (and A–B followed by B–C [25]) collisions. Consider the sequence of events where an A–C elastic collision is followed by a repulsive release. Let $V_i$ be the initial relative velocity, $\hat{n}k_i = \mu_i V_i$. Then $V_i$ is also the initial A–C relative velocity. If the A–C collision is elastic (in the A–C c.m. system) then $V_i$ is the final A–C relative velocity. Should the B–C bond snap without any energy release, $V_i$ would be the velocity with which C would recoil from AB and hence $k_C = \mu_i V_i / \mu_i = (\mu_i / \mu_1) k_1$. If there is a repulsive release, $k_C = (\mu_i / \mu_1) k_1 + I$. A similar reasoning would apply to a sequence of elastic collisions. The result

$$e^{1/2} = (\mu_i / \mu_1)^{1/2} E_T^{1/2} : \sin \beta R^{1/2}$$

(12)

does account, fig. 4, at least qualitatively, for the Rb +CH$_3$I experimental results, and for the higher ($e^{1/2}$ versus $E_T^{1/2}$) slope for the K+CH$_3$I experimental results. In practice, since most of the distribution is confined to the range $\lambda_T [(E_T^{1/2})^{1/2} - e^{1/2}]^2 \leq 1$, a plot of $\langle E_T^{1/2} \rangle$ (or of $Q$) versus $E_T$ will also yield an essentially straight line, as is often observed to be the case [1,5].

6. Concluding remarks

An information theoretic procedure based on a "constrained" momentum transfer has been introduced and applied to the analysis of energy disposal, with special reference to the role of the initial collision energy.

The momentum transfer constraint offers an operational distinction between attractive and repulsive release. In the latter case the $e^{1/2}$ versus $E_T^{1/2}$ plot has a finite intercept ($\sin \beta R^{1/2} = 0$) at $E_T = 0$. This criterion is identical to that used to classify potential energy surfaces [3,13]. Note however that for some mass combinations (e.g., Cl+HI) such that $\sin \beta$ is very small, a repulsive surface (as used in our trajectory computations) leads to recoil energy distribution which is quite similar (due to the low value of $\sin \beta R^{1/2}$) to those expected for attractive release, cf. fig. 4. In addition to the insight derived from the intercept, the slope of the $e^{1/2}$ versus $E_T^{1/2}$ plot provides information on the sequence of momentum transfers during the reactive collision. The accurate representation provided by $e = E_T$ for the non-reactive (trajectory-generated) distribution in Cl+HI, fig. 4, provides an additional demonstration of the validity of the present approach.

The very good approximation for the 3-D distribution via the collinear bias $(P_C(E_T^3)/P_C(E_T^0))$, fig. 3, should also be noted.
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References