

Chapter 9 Problems

1. The xyz and $x'y'z'$ reference frames of Figure 9.2 are respectively biased towards reactants and products. Can you think of an unbiased body-fixed reference frame?
2. The vector hierarchy used in Figure 9.3 was $\mathbf{k} \rightarrow \mathbf{k}' \rightarrow \mathbf{j}, \mathbf{j}'$. Redraw the figure using a different hierarchy $\mathbf{k} \rightarrow \mathbf{j} \rightarrow \mathbf{k}', \mathbf{j}'$.
3. Using theoretical methods, the authors of ref. [694] have associated a non-adiabatic effect in the dynamics of the $\text{H} + \text{H}_2$ reaction with product scattering into positive or negative “deflection angles”, see Figure 5 of that paper. Experimentally, positive and negative deflection angles cannot be distinguished – they correspond to the same scattering angle. Reactant or product polarization measurements, however, might allow experimental observation of the distinct reaction mechanisms. How?
Hint: see Problem 2.
4. When reaction (9.69) proceeds *via* mechanism a , the real PPs of reactants and products are those on the top row of Table 9.2. What are the values of their complex PPs?
5. A diatomic molecule is in a $j = 1$ rotational state. Calculate its density matrix, knowing that its non-vanishing complex polarization moments are $z_0^{(0)} = 1$, $z_0^{(2)} = \sqrt{1/10}$, $z_{+2}^{(2)} = i\sqrt{3/20}$, $z_{-2}^{(2)} = -i\sqrt{3/20}$. Is this molecule polarized? If so, how?
6. Using the data below, obtain mathematical expressions for the axial and rotational PDFs of the molecule of Problem 5. From the mathematical expressions can you tell how the molecule is polarized?

$$C_0^{\{0\}}(\Theta, \Phi) = 1, C_{2-}^{\{2\}}(\Theta, \Phi) = (3/4)^{1/2} \sin^2(\Theta) \sin(2\Phi),$$

$$\langle 11, 00 | 11 \rangle = 1, \langle 11, 20 | 11 \rangle = \sqrt{1/10}, \langle 10, 00 | 10 \rangle = 1, \langle 10, 20 | 10 \rangle = -\sqrt{2/5}.$$

7. In the trajectory of Figure 9.8 the internuclear axes of the reactant and product diatomics are oriented. But we have seen that, besides being incompatible with the axial portrait of Figure 9.12, this cannot happen. Show that indeed it does not. *Hint:* draw a new trajectory using reflection through the scattering plane. Can the new trajectory be more or less likely than the original?
8. Use Eqs. (9.18) and (9.22) to show that the complex polarization moments of a density matrix satisfy

$$a_q^{(k)} = (-1)^q [a_{-q}^{(k)}]^*$$

Hint: Use the fact that the density matrix is Hermitian (that is, $\langle jm_1 | \rho | jm_2 \rangle = \langle jm_2 | \rho | jm_1 \rangle^*$), and the formula^{239,647}

$$\langle jm_1, kq | jm_2 \rangle = (-1)^q \langle jm_2, k - q | jm_1 \rangle$$

9. Chemical reactions conserve parity. This implies⁶⁴⁵ that the elements of helicity-representation scattering matrices satisfy $\langle -\Omega' | S^J | \Omega \rangle = \langle -\Omega' | S^J | -\Omega \rangle$, which in turn implies that the density matrix of Eq. (9.36) satisfies

$$\langle \Omega_1 | \rho(\theta) | \Omega_2 \rangle = (-1)^{\Omega_2 - \Omega_1} \langle -\Omega_1 | \rho(\theta) | -\Omega_2 \rangle$$

Use this property to show that the polarization moments of $\rho(\theta)$ satisfy

$$S_q^{(k)}(\theta) = (-1)^{k+q} S_{-q}^{(k)}(\theta)$$

Hint: Use Eq. (9.18) and the formula^{239,647}

$$(-1)^{\Omega_2 - \Omega_1} \langle j\Omega_1, kq | j\Omega_2 \rangle = (-1)^{k+q} \langle j - \Omega_1, k - q | j - \Omega_2 \rangle$$

10. Combining the results of Problems 8 and 9, and noting that the symmetry properties obtained there are independent of whether the polarization moments are normalized PDDCSs, renormalized PDDCSs or PPs, we find that the intrinsic polarization moments of chemical reactions must satisfy

$$z_q^{(k)} = (-1)^q [z_{-q}^{(k)}]^* = (-1)^{k+q} z_{-q}^{(k)}$$

where $z_q^{(k)}$ stands for any of those polarization moments. Use these equalities to probe the following:

- (a) If k is even, then the complex polarization moments are actually real.
- (b) If k is even, then $z_{q-}^{\{k\}}$ polarization moments vanish.
- (c) If k is odd, then the complex polarization moments are actually pure imaginary.
- (d) If k is odd, then $z_0^{\{k\}}$ and $z_{q+}^{\{k\}}$ polarization moments vanish.

11. Conservation of parity also implies that the intrinsic rotational PDFs of chemical reactions must satisfy

$$P(\theta_j, \varphi_j) = P(\pi - \theta_j, \pi - \varphi_j)$$

Using this symmetry property and Eq. (9.32) – the classical expansion of rotational PDFs – show that the classical normalized PDDCSs satisfy

$$S_q^{(k)}(\theta) = (-1)^k [S_q^{(k)}(\theta)]^*$$

and therefore that they also follow the rules specified in items (a-d) of Problem

10. *Hint:* Use the following formula:⁶⁴⁷

$$C_{kq}(\pi - \theta, \pi - \varphi) = (-1)^k C_{kq}^*(\theta, \varphi)$$

12. Using the space-fixed frame described in Section 9.3.1.1, sketch an approach geometry one might observe at the start of a classical trajectory. How do the positions of the atoms depend on the collision parameters?
13. Show that the $|\Psi_{II}\rangle$ state of Eq. (9.81) is such that $A_0^{(1)} \neq 0$. Taking into consideration the conditions for intrinsic PP values determined in Problem 10, decide how the non-vanishing extrinsic $A_0^{(1)}$ will affect the reaction stereodynamics.
14. Prove the second equality of Eq. (9.78). *Hint:* First, rewrite Eq. (9.79) using, for each mechanism, $d\sigma/d\omega = (\sigma/2\pi)P(\theta)$. Next, expand $\text{Tr}(\rho_i \rho_e)$ using Eq. (9.21) twice; note that the expansion coefficients of $P_a(\theta)\rho_a$ are the normalized PDDCSs of mechanism a , and similarly for mechanisms b and c . Finally, use this formula:⁶⁴⁷

$$\sum_{m_1=-j}^j \sum_{m_2=-j}^j \frac{2k+1}{2j+1} \langle jm_1, KQ | jm_2 \rangle \langle jm_1, kq | jm_2 \rangle = \delta_{kK} \delta_{qQ}$$

15. Derive Eq. (9.84) from Eq. (9.78). *Hint:* Integration over θ transforms the complex normalized PDDCSs into complex PPs, see Eq. (9.25); integration over φ

averages the PPs with $q \neq 0$ to zero; the remaining PPs have $q = 0$ and are therefore real, see Eq. (9.11c).

16. This problem involves fairly long calculations requiring the values of CG coefficients and rotation matrix elements; the supplementary material contains a Maple® worksheet enabling automatic performance of all calculations. As the states and conditions involved can be changed by the user, this problem could be used for a class tutorial, with each student doing different but entirely analogous calculations.

As discussed in Chapter 12, an ultracold reaction proceeds only *via* the partial wave associated with $\ell = 0$. A consequence of this is that the scattering matrix elements are independent of reactant helicity.⁶⁹⁶ As the \mathbf{S} elements also satisfy $\langle \Omega' | \mathbf{S}^J | \Omega \rangle = \langle -\Omega' | \mathbf{S}^J | -\Omega \rangle$ (see Problem 9), for small j and j' values there are few \mathbf{S} elements one needs to consider, and fewer still whose values can be independently varied. The problem consists in choosing arbitrary values for the problem parameters and then analyzing the resulting stereodynamics.

- (a) Specify the values of j and j' . (The data in the worksheet allows for calculations involving $j \leq 5$ and $j' \leq 5$.)
- (b) Noting that $\ell = 0$ condition implied $\mathbf{j} = \mathbf{J}$, decide what \mathbf{S} elements can be independently varied, and then assign an arbitrary complex value to each of them. (The worksheet will check whether your specification allows for a full, unique specification of the required \mathbf{S} elements, and then scale them so that $\sigma_{\text{ur}} = 10 \text{ \AA}^2$.)
- (c) Choose a reference frame for the stereodynamical analysis.
- (d) Follow the instructions in the worksheet to calculate the following:
- DCS of the reaction involving unpolarized reactants, $d\sigma_{\text{ur}}/d\omega$.
 - Intrinsic density matrices of reactants and products.
 - Intrinsic real renormalized PDDCS of reactants and products and the associated stereodynamical portraits.
 - Intrinsic real PPs of reactants and products and the associated portraits.
- (e) From this data, rationalize the stereodynamics and comment on the possibilities of ICS and DCS control *via* reactant polarization. *Hint:* Think about the consequences of the $\ell = 0$ restriction for the approach direction

from the viewpoint of reactive collisions, and also about the consequences of $\mathbf{j} = \mathbf{J}$ and total angular momentum conservation.

- (f) Specify a set of directions for \mathbf{r} alignment, and then use the worksheet to calculate the resulting ICSs and DCSs. Are the results consistent with your answer to item (e)?
- (g) Use the worksheet to disentangle the independent reaction mechanisms and calculate the stereodynamical properties of each of them.
- (h) Rationalize the stereodynamics of the various independent mechanisms.
Hint: Rather than thinking about the mechanisms in terms of classical trajectories, think about angular momentum conservation.