Chapter 5 Problems

1. Compare the collision systems $H_2(v = 1) + H_2(v = 0)$ and $D_2(v = 1) + D_2(v = 0)$ in the case of a pure gas at identical thermal and density conditions.
   (a) Compare the coupling, as predicted by Eq. (5.2), between the vibrational and translational motions of both systems. Use Ehrenfest's adiabatic principle to predict the ratio of the relaxation rates for $v = 1$ vibrational-to-translational energy transfer for a pure gas of H_2 molecules and that in a pure gas of D_2 molecules.
   (b) Employ the Landau-Teller result of Eq. (5.4) to calculate this ratio directly.
   (c) Calculate this ratio using Eq. (5.4) in the case that the collider gases, $H_2(v = 0)$ and $D_2(v = 0)$, are replaced by Ar.
2. (a) Derive Eq. (5.14).
   (b) Derive Eq. (5.16).
   (c) Consider a collision between an incoming hard-sphere-like molecule with an initially stationary atom. Show that to first order the amount of translational energy ΔE_t that is transferred upon collision is at least $\Delta E_\mathrm{t} = \frac{1}{2} m_1 v_1^2 (1 - F)(1 - D^2/4)$ (see Eq. (1.24) from ref. [427]). Here m_1 and m_2 denote, respectively, the mass of the molecule and the initially stationary atom, and v_1 is the laboratory velocity of the incoming molecule. D corresponds to the mass defect, defined as $(m_1 - m_2)/m_1$, and F is the fraction of all the hard sphere collisions with total collision cross section πR_S^2 that contribute to ΔE_t (see Eq. (5.23)). (Note that this simple equation implies that if one has $D = 0$ and $b = 0$ all of the initial kinetic energy, $\frac{1}{2} m_1 v_1^2$, is transferred to the atom, and, as follows also directly from Eq. (5.16), this leads to $F = 0$.)
   (d) In the case of a mass mismatch, D = 10%, calculate the maximal fraction of the incoming kinetic energy (*i.e.* at F = 0 which corresponds to b = 0 collision) that can be transferred to the atom. Next show that the fraction of collisions $1 - F$ that transfer more than 99% of the incoming translational energy of the molecule with D = 10% is about 1%. (Note that if the incoming kinetic energy of the molecules is just low enough that these 1% of molecules become

trapped, the other 99% will be ejected from the trap. A value of 1% for the fraction of the incoming molecules to remain in the trap strongly suggests that such trapping experiments are feasible for kinematically slowed HBr that is subsequently trapped in a Rb magneto-optical trap[425] (see Study Box 12.1).)

3. Show that Eqs. (5.26) and (5.27) imply that $\boldsymbol{j} \cdot \hat{\boldsymbol{a}} = \boldsymbol{j}' \cdot \widehat{\boldsymbol{a}'}$ or $(\boldsymbol{j}' - \boldsymbol{j}) \cdot \hat{\boldsymbol{a}} = \Delta\boldsymbol{j} \cdot \hat{\boldsymbol{a}} = 0$, *i.e.* the projection of the rotational angular momentum onto kinematic apse remains conserved for a hard shell type of collision. (Note that rotationally inelastic state-to-state differential scattering experiments probing the alignment vector, $\boldsymbol{j}'$, of the outgoing molecule for the closed shell Ne-Na_2 system,[344] and for the open shell rare gas-NO system, have been shown to conform to this propensity rule in the quantum mechanical limit.[428-430])
4. Derive Eqs. (5.28) to (5.35), starting from the conservation of energy and angular momentum, Eqs. (5.26) and (5.27).
5. Explain why there is a summation over two terms in Eq. (5.64).