Rotational Spectra of Molecules

In this problem, we will explore the quantum mechanical rotation of a polyatomic molecule. Since transitions between these states are observed easily through chemical spectroscopy, such an understanding is very important and also allows for a good experimental check of quantum mechanics.

Let $\mathbf{x}_i$ be the position of atom i, and $\mathbf{p}_i$ be the momentum of atom i. As usual, assume the commutation relations:

$$[(x_m)_i, (x_n)_j] = [(p_m)_i, (p_n)_j] = 0,$$
$$[(x_m)_i, (p_n)_j] = \mathrm{i}\delta_{ij}\delta_{mn}.$$

Also, define the molecule's angular momentum as

$$\mathbf{J} = \sum_i \mathbf{x}_i \times \mathbf{p}_i.$$

(a) Verify that $[J^2, \mathbf{J}] = \mathbf{0}$ and $[J_i, J_j] = \mathrm{i}\epsilon_{ijk}J_k$.

(b) Let $\mathbf{v}_1$ and $\mathbf{v}_2$ be two fixed vectors in position space. Show that

$$[\mathbf{J}\cdot\mathbf{v}_1, \mathbf{J}\cdot\mathbf{v}_2] = \mathrm{i}\mathbf{J}\cdot(\mathbf{v}_1\times\mathbf{v}_2).$$

(c) Calculate $[J_i, (x_m)_j]$ and $[J_i, (p_m)_j]$.

(d) Now let

$$\mathbf{w}_\alpha = \sum_i a_{\alpha,i}\mathbf{x}_i$$

for $\alpha = 1, 2$. Show that

$$[\mathbf{J}\cdot\mathbf{w}_1, \mathbf{J}\cdot\mathbf{w}_2] = -\mathrm{i}\mathbf{J}\cdot(\mathbf{w}_1\times\mathbf{w}_2).$$

Why is this result different from that in part (b)?

Now, let us assume that the Hamiltonian for our molecule is

$$H = \frac{J_1^2}{2I_1} + \frac{J_2^2}{2I_2} + \frac{J_3^2}{2I_3}$$

for arbitrary I_1, I_2 and I_3. This is the usual Hamiltonian for a rigid body. The only issue is that J_1, J_2 and J_3 are components of the angular momentum in a reference frame which rotates along with the body itself! Luckily, we just so happen to have developed the technology to deal with this situation. Let's denote $\mathbf{e}_\mu$ ($\mu = 1, 2, 3$) to be the basis vectors fixed along the principal axes of the molecule:[1] thus, $\mathbf{e}_\mu\cdot\mathbf{e}_\nu = \delta_{\mu\nu}$. We also define $J_\mu \equiv \mathbf{J}\cdot\mathbf{e}_\mu$.

(e) Calculate $[J_\mu, J_\nu]$ and $[J^2, J_\mu]$ and comment on the results.

(f) Let $\mathbf{e}_z$ be some vector fixed in the laboratory frame, and $J_z \equiv \mathbf{J}\cdot\mathbf{e}_z$. Show that $[J_3, J_z] = 0$. What is the Hilbert space for the quantum mechanical problem?

[1] This means that if we rotate about axis $\mathbf{e}_\mu$, the moment of inertia is I_μ.

We are finally ready to compute the quantum mechanical energies of our molecule (with respect to rotation).

(g) Suppose that $I_1 = I_2 = I_3$. What are the eigenvalues of H, and their degeneracies?

(h) Suppose that $I_1 = I_2 \neq I_3$. What are the eigenvalues of H, and their degeneracies? Comment on what you observe for the case $I_1 < I_3$, as well as the case $I_1 > I_3$.

Although both of the cases above have exact solutions, the generic case $I_1 \neq I_2 \neq I_3$ does not have exact solutions, in general. However, that does not mean we can't keep thinking about this case!

(i) Show that we can still find the exact energy spectrum of the molecule when the total angular momentum is either $j = 0$ or $j = 1$.

(j) Explain how the case of $j > 1$ reduces to computing the eigenvalues of a finite dimensional matrix, which you can explicitly find. Write some numerical code to evaluate this determinant explicitly for arbitrary I_1, I_2 and I_3, and look at the sample case $I_1 = 2I_2 = 3I_3$. Check that the $j = 0$ and $j = 1$ states agree with what you found, and then determine numerically the eigenvalues for $j = 2$. Be sure to check (and show) that the code works for larger values of j by numerically determining some of the exact spectra you found earlier.