Ammonia

Problem: **Ammonia molecule: position of nitrogen atom.**
In state $|u\rangle$, the nitrogen atom is positioned a distance s above the plane of three hydrogen atoms; in state $|d\rangle$ it is positioned the same distance below. The position of the nitrogen atom is thus represented by the operator

$$\hat{z}_N = (+s)|u\rangle\langle u| + (-s)|d\rangle\langle d| \tag{1}$$

Write the matrix representation of the $\hat{z}_N$ operator in the basis $\{|u\rangle, |d\rangle\}$ and in the basis $\{|e_1\rangle, |e_2\rangle\}$. What is the commutator $[\hat{z}_N, \hat{H}]$?

Solution: In the $\{|u\rangle, |d\rangle\}$ basis,

$$\hat{z}_N \doteq \begin{pmatrix} +s & 0 \\ 0 & -s \end{pmatrix}. \tag{2}$$

In the $\{|e_1\rangle, |e_2\rangle\}$ basis,

$$\hat{z}_N \doteq \begin{pmatrix} \langle e_1|\hat{z}_N|e_1\rangle & \langle e_1|\hat{z}_N|e_2\rangle \\ \langle e_2|\hat{z}_N|e_1\rangle & \langle e_2|\hat{z}_N|e_2\rangle \end{pmatrix}. \tag{3}$$

What are these four matrix elements? The first is

$$\langle e_1|\hat{z}_N|e_1\rangle = (+s)\langle e_1|u\rangle\langle u|e_1\rangle + (-s)\langle e_1|d\rangle\langle d|e_1\rangle.$$

But the four amplitudes on the right were worked out in the text when we found the energy eigenvectors:

$$\begin{aligned} \langle e_1|\hat{z}_N|e_1\rangle &= (+s)\langle e_1|u\rangle\langle u|e_1\rangle + (-s)\langle e_1|d\rangle\langle d|e_1\rangle \\ &= (+s)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + (-s)\left(-\frac{e^{+i\phi}}{\sqrt{2}}\right)\left(-\frac{e^{-i\phi}}{\sqrt{2}}\right) \\ &= s\left(\frac{1}{2} - \frac{1}{2}\right) \\ &= 0 \end{aligned} \tag{4}$$

The value of this matrix element makes sense: It is the mean value of of the nitrogen atom's position in state $|e_1\rangle$. In this state, the atom doesn't have a position, but if the position is measured it has probability $\frac{1}{2}$ of being up and $\frac{1}{2}$ of being down, so the mean value is zero.

The upper right matrix element is

$$\begin{aligned} \langle e_1|\hat{z}_N|e_2\rangle &= (+s)\langle e_1|u\rangle\langle u|e_2\rangle + (-s)\langle e_1|d\rangle\langle d|e_2\rangle \\ &= (+s)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + (-s)\left(\frac{-e^{+i\phi}}{\sqrt{2}}\right)\left(\frac{e^{-i\phi}}{\sqrt{2}}\right) \\ &= s\left(\frac{1}{2} + \frac{1}{2}\right) \\ &= s \end{aligned} \tag{5}$$

It is always harder to make sense of off-diagonal matrix elements, and I have no insight into why this element takes this particular value. But at least it has the correct dimensions for a position!

The lower left matrix element is

$$\begin{aligned}
\langle e_2|\hat{z}_N|e_1\rangle &= (+s)\langle e_2|u\rangle\langle u|e_1\rangle + (-s)\langle e_2|d\rangle\langle d|e_1\rangle \\
&= (+s)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + (-s)\left(\frac{e^{+i\phi}}{\sqrt{2}}\right)\left(-\frac{e^{-i\phi}}{\sqrt{2}}\right) \\
&= s\left(\frac{1}{2}+\frac{1}{2}\right) \\
&= s
\end{aligned} \tag{6}$$

And finally

$$\begin{aligned}
\langle e_2|\hat{z}_N|e_2\rangle &= (+s)\langle e_2|u\rangle\langle u|e_2\rangle + (-s)\langle e_2|d\rangle\langle d|e_2\rangle \\
&= (+s)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + (-s)\left(\frac{e^{+i\phi}}{\sqrt{2}}\right)\left(\frac{e^{-i\phi}}{\sqrt{2}}\right) \\
&= s\left(\frac{1}{2}-\frac{1}{2}\right) \\
&= 0
\end{aligned} \tag{7}$$

with the same interpretation as equation (4).

So, in the $\{|e_1\rangle, |e_2\rangle\}$ basis the operator $\hat{z}_N$ is represented by

$$\hat{z}_N \doteq \begin{pmatrix} 0 & s \\ s & 0 \end{pmatrix}. \tag{8}$$

To represent a physical measurement, a matrix must be Hermitian, and this one is.

I could work out the commutator $[\hat{z}_N, \hat{H}]$ in the $\{|u\rangle, |d\rangle\}$ basis, where

$$\hat{z}_N \doteq \begin{pmatrix} +s & 0 \\ 0 & -s \end{pmatrix} \quad \text{and} \quad \hat{H} \doteq \begin{pmatrix} E & Ae^{i\phi} \\ Ae^{-i\phi} & E \end{pmatrix},$$

or in the $\{|e_1\rangle, |e_2\rangle\}$ basis, where

$$\hat{z}_N \doteq \begin{pmatrix} 0 & s \\ s & 0 \end{pmatrix} \quad \text{and} \quad \hat{H} \doteq \begin{pmatrix} E-A & 0 \\ 0 & E+A \end{pmatrix},$$

or using outer product forms like equation (1). Each of the three strategies will produce the same answer (provided no mistakes are made) but it's pretty clear that the second strategy is easiest, because of all the zero elements in the matrices. (Also, all the matrix elements are pure real.) So in the $\{|e_1\rangle, |e_2\rangle\}$ basis

$$\hat{z}_N\hat{H} \doteq \begin{pmatrix} 0 & s \\ s & 0 \end{pmatrix}\begin{pmatrix} E-A & 0 \\ 0 & E+A \end{pmatrix} = \begin{pmatrix} 0 & s(E+A) \\ s(E-A) & 0 \end{pmatrix}$$

while

$$\hat{H}\hat{z}_N \doteq \begin{pmatrix} E-A & 0 \\ 0 & E+A \end{pmatrix} \begin{pmatrix} 0 & s \\ s & 0 \end{pmatrix} = \begin{pmatrix} 0 & s(E-A) \\ s(E+A) & 0 \end{pmatrix}$$

so

$$\hat{z}_N\hat{H} - \hat{H}\hat{z}_N \doteq \begin{pmatrix} 0 & 2sA \\ -2sA & 0 \end{pmatrix} \tag{9}$$

or

$$[\hat{z}_N, \hat{H}] = 2sA\left(|e_1\rangle\langle e_2| - |e_2\rangle\langle e_1|\right). \tag{10}$$

If you used the $\{|u\rangle, |d\rangle\}$ basis you instead found

$$\hat{z}_N\hat{H} \doteq \begin{pmatrix} sE & sAe^{i\phi} \\ -sAe^{-i\phi} & -sE \end{pmatrix} \quad \text{and} \quad \hat{H}\hat{z}_N \doteq \begin{pmatrix} sE & -sAe^{i\phi} \\ sAe^{-i\phi} & -sE \end{pmatrix}$$

so

$$\hat{z}_N\hat{H} - \hat{H}\hat{z}_N \doteq \begin{pmatrix} 0 & 2sAe^{i\phi} \\ -2sAe^{-i\phi} & 0 \end{pmatrix} \tag{11}$$

or

$$[\hat{z}_N, \hat{H}] = 2sA\left(e^{i\phi}|u\rangle\langle d| - e^{-i\phi}|d\rangle\langle u|\right). \tag{12}$$

The textbook expressions for $|e_1\rangle$ and $|e_2\rangle$ in terms of $|u\rangle$ and $|d\rangle$ show that expressions (10) and (12) are equal.

The important thing is that $\hat{z}_N$ and $\hat{H}$ do *not* commute: if they commuted the nitrogen atom position would be conserved, but in fact we know that it changes with time because of the tunneling.

⟦*Grading:* 1 point for each of equations (2) through (8); 3 points for any one of equations (9) through (12).⟧

Problem: **Ammonia molecule in an electric field**
Find the eigenvalues of

$$\begin{pmatrix} E + p\mathcal{E} & Ae^{i\phi} \\ Ae^{-i\phi} & E - p\mathcal{E} \end{pmatrix}.$$

Solution:

$$\begin{aligned}
\det \begin{pmatrix} E + p\mathcal{E} - \lambda & Ae^{i\phi} \\ Ae^{-i\phi} & E - p\mathcal{E} - \lambda \end{pmatrix} &= 0 \\
(E + p\mathcal{E} - \lambda)(E - p\mathcal{E} - \lambda) - A^2 &= 0 \\
\lambda^2 - \lambda(E + p\mathcal{E} + E - p\mathcal{E}) + (E + p\mathcal{E})(E - p\mathcal{E}) - A^2 &= 0 \\
\lambda^2 - 2E\lambda + (E^2 - (p\mathcal{E})^2 - A^2) &= 0
\end{aligned}$$

Solve through the quadratic equation

$$\begin{aligned}
\lambda &= \tfrac{1}{2}\left[2E \pm \sqrt{4E^2 - 4(E^2 - (p\mathcal{E})^2 - A^2)}\right] \\
&= E \pm \sqrt{E^2 - (E^2 - (p\mathcal{E})^2 - A^2)} \\
&= E \pm \sqrt{(p\mathcal{E})^2 + A^2}.
\end{aligned}$$

Sure enough, when $\mathcal{E} = 0$, this reduces to the result $e = E \pm A$ in the text.

⟦*Grading:* 3 points for setting up the determinate equation; 3 points for reducing it to a quadratic; 3 points for solving that quadratic equation; 1 point for the $\mathcal{E} = 0$ statement.⟧