Theoretical Physics 2019/20 — Solution of Problem QT2.5

(a) (i) We only need to calculate $\hat{H}|+\rangle$ and $\hat{H}|-\rangle$. Let us start with $\hat{H}|+\rangle$.

$$\hat{H}|+\rangle = (E_0|A\rangle\langle A| + \Delta|A\rangle\langle B| + \Delta|B\rangle\langle A| + E_0|B\rangle\langle B|)\,(|A\rangle + |B\rangle)/\sqrt{2}.$$

Step by step, for clarity:

$$\begin{aligned}\hat{H}|+\rangle &= [\,E_0|A\rangle\langle A|\,(|A\rangle + |B\rangle) + \Delta|A\rangle\langle B|\,(|A\rangle + |B\rangle) + \\ &\qquad \Delta|B\rangle\langle A|\,(|A\rangle + |B\rangle) + E_0|B\rangle\langle B|\,(|A\rangle + |B\rangle)\,]/\sqrt{2} \\ &= [\,E_0|A\rangle\langle A|A\rangle + E_0|A\rangle\langle A|B\rangle + \Delta|A\rangle\langle B|A\rangle + \Delta|A\rangle\langle B|B\rangle + \\ &\qquad \Delta|B\rangle\langle A|A\rangle + \Delta|B\rangle\langle A|B\rangle + E_0|B\rangle\langle B|A\rangle + E_0|B\rangle\langle B|B\rangle\,]/\sqrt{2}.\end{aligned}$$

Since $\langle A|A\rangle = \langle B|B\rangle = 1$ and $\langle A|B\rangle = \langle B|A\rangle = 0$,

$$\begin{aligned}\hat{H}|+\rangle &= [\,E_0|A\rangle + 0 + 0 + \Delta|A\rangle + \Delta|B\rangle + 0 + 0 + E_0|B\rangle\,]/\sqrt{2} \\ &= (E_0 + \Delta)\,(|A\rangle + |B\rangle)/\sqrt{2} \\ &= (E_0 + \Delta)\,|+\rangle,\end{aligned}$$

which shows that, indeed, $|+\rangle$ is an eigenvector of $\hat{H}$ and the corresponding eigenvalue is $E_0 + \Delta$.

The above calculation could have been kept shorter by using the orthonormality of $|A\rangle$ and $|B\rangle$ right from the start. Doing so for $|-\rangle$ yields

$$\begin{aligned}\hat{H}|-\rangle &= (E_0|A\rangle\langle A| + \Delta|A\rangle\langle B| + \Delta|B\rangle\langle A| + E_0|B\rangle\langle B|)\,(|A\rangle - |B\rangle)/\sqrt{2} \\ &= [\,E_0|A\rangle - 0 + 0 - \Delta|A\rangle + \Delta|B\rangle - 0 + 0 - E_0|B\rangle\,]\sqrt{2} \\ &= (E_0 - \Delta)\,(|A\rangle - |B\rangle)/\sqrt{2} \\ &= (E_0 - \Delta)\,|-\rangle,\end{aligned}$$

which shows that, indeed, $|-\rangle$ is an eigenvector of $\hat{H}$ and the corresponding eigenvalue is $E_0 - \Delta$.

[1 mark]

(ii) $\hat{H}$ reduces to $E_0|A\rangle\langle A| + E_0|B\rangle\langle B|$ when $\Delta = 0$. Then $\hat{H}|A\rangle = E_0|A\rangle + 0 = E_0|A\rangle$, and, similarly, $\hat{H}|B\rangle = E_0|B\rangle$. Thus $|A\rangle$ and $|B\rangle$ are eigenvectors of $\hat{H}$ when $\Delta = 0$ and the corresponding eigenvalue is E_0 both for $|A\rangle$ and $|B\rangle$.

However, when $\Delta \neq 0$,

$$\begin{aligned}\hat{H}|A\rangle &= (E_0|A\rangle\langle A| + \Delta|A\rangle\langle B| + \Delta|B\rangle\langle A| + E_0|B\rangle\langle B|)\,|A\rangle \\ &= E_0|A\rangle + \Delta|B\rangle,\end{aligned}$$

which is not the product of $|A\rangle$ by a scalar. Similarly,

$$\begin{aligned}\hat{H}|B\rangle &= (E_0|A\rangle\langle A| + \Delta|A\rangle\langle B| + \Delta|B\rangle\langle A| + E_0|B\rangle\langle B|)\,|B\rangle \\ &= \Delta|A\rangle + E_0|B\rangle,\end{aligned}$$

which is not the product of $|A\rangle$ by a scalar. Thus neither $|A\rangle$ nor $|B\rangle$ is an eigenvector of $\hat{H}$ when $\Delta \neq 0$. (The same can be concluded immediately from the result of part (i): $|A\rangle$ and $|B\,\rangle$ are linear combinations of the eigenvectors $|+\rangle$ and $|-\rangle$; however, as $|+\rangle$ and $|-\rangle$ belong to two different eigenvalues when $\Delta \neq 0$, such linear combinations are not eigenvectors of $\hat{H}$.)

[2 marks]

The splitting is due to the presence of an effective potential barrier impeding but not preventing the motion of the nitrogen atom across the plane of the hydrogen atoms (this barrier originates from the electrostatic repulsion between the different atomic nuclei). If the nitrogen atom was a classical particle, this barrier would confine it to be either above or below the plane of the hydrogen atoms (taking this plane to be horizontal, for simplicity). As a quantum particle, however, the nitrogen atom can tunnel through this barrier.

If the barrier was infinite, the atom's wave function (treating the atom as a point particle) would vanish inside it. One could thus have an energy eigenstate A where the atom would have a zero probability to be below that plane and an energy eigenstate B where it would have a zero probability to be above it. The respective wave functions $\psi_A(z)$ and $\psi_B(z)$ would be non-zero only above (state A) or below (state B) the hydrogen plane. As an infinite barrier is impenetrable, a molecule in state A would stay in that state forever, and similarly for a molecule in state B. By symmetry, the energy eigenfunctions $\psi_A(z)$ and $\psi_B(z)$ would correspond to a same energy, and so would any linear combination of these two eigenfunctions.

However, the actual barrier is not infinite and the nitrogen atom has a non-zero probability to tunnel through it. The wave function characterizing its position can therefore be non-zero inside this barrier. Suppose that $\psi_A(z)$ and $\psi_B(z)$ would be two energy eigenfunctions corresponding to a same eigenenergy but to different probabilities that the nitrogen atom is above or below the hydrogen plane. A linear combination of these two wave functions should also be an energy eigenfunction corresponding to that eigenenergy. However, here there is an impossibility: Consider the linear combinations $\phi_\pm(z) = \alpha\psi_A(z) \pm \beta\psi_B(z)$ with $\alpha = \psi_B(z_0)$ and $\beta = \psi_A(z_0)$, where z_0 is a position where the potential barrier is particularly strong and where neither $\psi_A(z_0)$ nor $\psi_B(z_0)$ is zero. Thus $|\phi_-(z)|^2 = 0$ and $|\phi_+(z)|^2 \neq 0$ at $z = z_0$, which means that in the state $\phi_-(z)$, the nitrogen atom has a much lower probability of experiencing a strong repulsion from the hydrogen atoms than in the state $\phi_+(z)$. Therefore the molecule cannot have the same energy in these two states. Hence, if the potential barrier is finite, it is incorrect to assume that there may exist two energy eigenfunctions $\psi_A(z)$ and $\psi_B(z)$ corresponding to a same eigenenergy but different probabilities for the nitrogen atom to be above or below the hydrogen plane. Instead, energy eigenfunctions correspond to different energies according to whether they describe states in which the nitrogen atom has a smaller or larger probability to be inside the barrier.

In the model, $\Delta = 0$ (no energy splitting) corresponds to the case of an infinite potential barrier in the hydrogen plane, and $\Delta \neq 0$ corresponds to the actual molecule where the potential barrier is not infinite and the nitrogen atom can tunnel through it.

(b) First, $|+\rangle$ and $|-\rangle$ are orthogonal:

$$\langle +|-\rangle = (\,\langle +|+\rangle - \langle +|-\rangle + \langle -|+\rangle - \langle -|-\rangle\,)/2 = (1 - 0 + 0 - 1)/2 = 0.$$

Second, $|+\rangle$ and $|-\rangle$ are normalized:

$$\begin{aligned}\langle +|+\rangle &= (\,\langle +|+\rangle + \langle +|-\rangle + \langle -|+\rangle + \langle -|-\rangle\,)/2 = (1 + 0 + 0 + 1)/2 = 1,\\ \langle -|-\rangle &= (\,\langle +|+\rangle - \langle +|-\rangle - \langle -|+\rangle + \langle -|-\rangle\,)/2 = (1 - 0 - 0 + 1)/2 = 1.\end{aligned}$$

Third, $|+\rangle$ and $|-\rangle$ are linearly independent since they are orthogonal, and given that the Hilbert space spanned by $|A\rangle$ and $|B\rangle$ is a space of dimension 2, any set of two linearly independent vector belonging to that space forms a basis for that space.

[1 mark]

(c) We start with the representation in the $\{|A\rangle, |B\rangle\}$ basis. As found in Part (a)(ii),

$$\hat{H}|A\rangle = E_0|A\rangle + \Delta|B\rangle$$

and

$$\hat{H}|B\rangle = \Delta|A\rangle + E_0|B\rangle.$$

Thus $\langle A|\hat{H}|A\rangle = E_0$, $\langle A|\hat{H}|B\rangle = \Delta$, $\langle B|\hat{H}|A\rangle = \Delta$ and $\langle B|\hat{H}|B\rangle = E_0$.

For the representation in the $\{|+\rangle, |-\rangle\}$ basis, we use $\hat{H}|+\rangle = (E_0 + \Delta)|+\rangle$ and $\hat{H}|-\rangle = (E_0 - \Delta)|-\rangle$, as well as the orthonormality of $|+\rangle$ and $|-\rangle$:

$$\begin{aligned}\langle +|\hat{H}|+\rangle &= (E_0 + \Delta)\langle +|+\rangle = E_0 + \Delta,\\ \langle +|\hat{H}|-\rangle &= (E_0 - \Delta)\langle +|-\rangle = 0\\ \langle -|\hat{H}|+\rangle &= (E_0 + \Delta)\langle -|+\rangle = 0\\ \langle -|\hat{H}|-\rangle &= (E_0 - \Delta)\langle -|-\rangle = E_0 + \Delta.\end{aligned}$$

[2 marks]

(d) The eigenvalues of H are the values of λ such that

$$\begin{vmatrix} E_0 - \lambda & \Delta \\ \Delta & E_0 - \lambda \end{vmatrix} = 0.$$

I.e., $(E_0 - \lambda)^2 - \Delta^2 = 0$, which means that $E_0 - \lambda = \pm\Delta$. Thus $\lambda = E_0 \pm \Delta$, in agreement with the eigenenergies found in part (a)(i).

The required eigenvectors are found by solving the equation

$$\begin{pmatrix} E_0 - \lambda & \Delta \\ \Delta & E_0 - \lambda \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 0$$

with $\lambda = E_0 \pm \Delta$.

For $\lambda = E_0 + \Delta$, we have

$$\begin{pmatrix} -\Delta & \Delta \\ \Delta & -\Delta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 0,$$

which means that $x = y$. Taking $x = y = 1/\sqrt{2}$ gives the eigenvector

$$\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix},$$

which is the same as the column vector representing $|+\rangle$ in the $\{|A\rangle, |B\rangle\}$ basis ($\langle A|+\rangle = 1/\sqrt{2}$ and $\langle B|+\rangle = 1/\sqrt{2}$).

For $\lambda = E_0 - \Delta$, we have

$$\begin{pmatrix} \Delta & \Delta \\ \Delta & \Delta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 0,$$

which means that $x = -y$. Taking $x = 1/\sqrt{2}$ and $y = -1/\sqrt{2}$ gives the eigenvector

$$\begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix},$$

which is the same as the column vector representing $|-\rangle$ in the $\{|A\rangle, |B\rangle\}$ basis ($\langle A|-\rangle = 1/\sqrt{2}$ and $\langle B|-\rangle = -1/\sqrt{2}$).

[2 marks]

The eigenvalues of H' can be found by inspection: Since this matrix is diagonal, its eigenvalues are its diagonal elements. The eigenvalues $E_0 \pm \Delta$ correspond, respectively, to eigenvectors of the form

$$\begin{pmatrix} x \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ x \end{pmatrix},$$

where x is non-zero. For instance,

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

which are the column vectors representing, respectively, $|+\rangle$ and $|-\rangle$ in the $\{|+\rangle, |-\rangle\}$ basis ($\langle +|+\rangle = 1$ and $\langle -|+\rangle = 0$, and similarly for $|-\rangle$).

[2 marks]