

## Hour Exam 2 Solution

1. (10 pts) **Calculate** the energy in Joules required to excite an electron in the hydrogen atom from the  $n = 2$  to  $n = 4$  state, given that the Rydberg constant converted to Joule units is  $\approx 2.18 \cdot 10^{-18} J$ .

**Solution:**

To find the energy required to excite an electron from the  $n=1$  to  $n=2$  level in the hydrogen atom, we use

$$\begin{aligned} \Delta E &= E_2 - E_1 = hcR \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 2.18 \cdot 10^{-18} \left( \frac{1}{4} - \frac{1}{16} \right) = 4.087 \times 10^{-19} J \end{aligned} \quad (1)$$

2. (10 pts) **Show** that the Gaussian stationary state  $\psi(x) \sim e^{-m\omega x^2/2\hbar}$  of the vibrating molecule that we derived in lecture really is the lowest energy state, or 'ground state': the Heisenberg principle forbids the wavefunction from having a smaller  $\Delta x$  and 'squeezing down further' in energy.

**[Hint:** The lowering operator is  $\hat{a} = \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)$ , and you should remember what  $\hat{p} = ?$  ]

**Solution:**

Our approach should be to show that the ground state cannot be lowered anymore, that is,

$$\hat{a}\psi_0(x) = 0$$

You should remember that  $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ .

$$\therefore \hat{a} = \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(\hat{x} + \frac{\hbar}{m\omega} \frac{\partial}{\partial x}\right)$$

Ignoring the normalization factor for the proof, we have

$$\begin{aligned} \hat{a}\psi_0 &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left[ x e^{-m\omega x^2/2\hbar} + \frac{\hbar}{m\omega} \left(-\frac{m\omega}{2\hbar} 2x e^{-m\omega x^2/2\hbar}\right) \right] \\ &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left[ x e^{-m\omega x^2/2\hbar} - x e^{-m\omega x^2/2\hbar} \right] = 0 \end{aligned}$$

3. (15 pts) If  $Y_{2,-2} \sim \sin^2(\theta)e^{-2i\theta}$  and  $Y_{2,+2} \sim \sin^2(\theta)e^{+2i\theta}$  are degenerate eigenfunctions of the Hamiltonian  $\hat{H}_{rot}$  with eigenvalue  $E_{2,\pm 2} = \frac{6\hbar^2}{2mR^2}$ ,

a) **Write down** the real function  $d_{xy}(\theta, \phi) \sim i(Y_{2,+2} - Y_{2,-2})$ , and **prove** that it is also an eigenfunction of  $\hat{H}_{rot}$ .

**Solution:**

$$\begin{aligned} d_{xy}(\theta, \phi) \sim i(Y_{2,+2} - Y_{2,-2}) &= i \sin^2(\theta) (e^{2i\phi} - e^{-2i\phi}) \\ &= i \sin^2(\theta) [2i \sin(2\phi)] \\ &= -2 \sin^2(\theta) \sin(2\phi) \end{aligned}$$

To prove  $d_{xy}$  is an eigenfunction of  $\hat{H}_{rot}$ , apply the Hamiltonian on the function:

$$\begin{aligned} \hat{H}_{rot} d_{xy}(\theta, \phi) &\sim \hat{H}_{rot} [i(Y_{2,+2} - Y_{2,-2})] \\ &= \frac{6\hbar^2}{2mR^2} [i(Y_{2,+2} - Y_{2,-2})] \\ &= \frac{6\hbar^2}{2mR^2} d_{xy}(\theta, \phi) \end{aligned}$$

Since applying  $\hat{H}_{rot}$  on  $d_{xy}(\theta, \phi)$  yields some number times  $d_{xy}(\theta, \phi)$ , it is proven that  $d_{xy}$  is an eigenfunction of  $\hat{H}_{rot}$ .

b) **Plot** a polar plot of  $d_{xy}(\theta, \phi)$  in the x-y plane ( $\theta = \pi/2$ , plot as function of  $\phi$ ). Cross-hatch the negative lobes of the function.

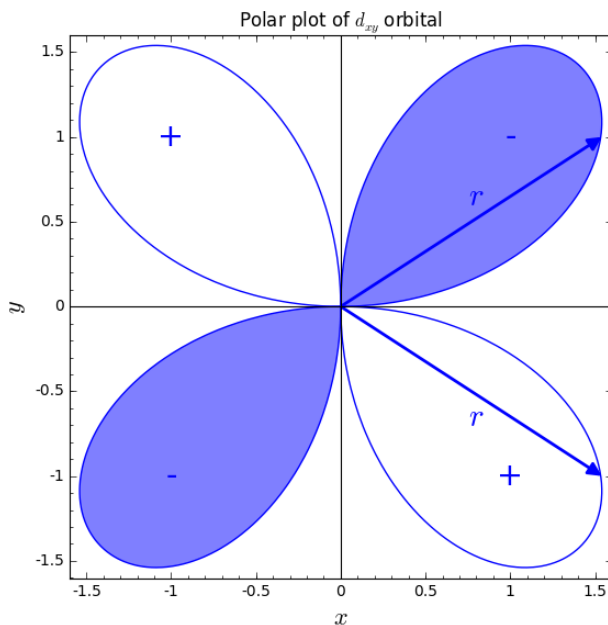
**Solution:**

Although the plot below is generated by a computer program, it can be easily done by hand by making a table of values:

$\phi$ (rad)	0	$\pi/4$	$\pi/2$	$3\pi/4$	$\pi$	$5\pi/4$	$3\pi/2$	$7\pi/4$	$2\pi$
$d_{xy} \sim -2 \sin^2\left(\frac{\pi}{2}\right) \sin 2\phi$ $= -2 \sin 2\phi$ $= r$	0	-2	0	2	0	-2	0	2	0

$|r|$  is the distance from the origin with an angle  $\phi$  from the x-axis. When  $r$  is negative, it means that the lobe is negative.

1 pt awarded for an incorrect plot. 0 pt for blank.



c) Given the trigonometric identity  $\sin 2\phi \sim \sin \phi \cos \phi$ , and knowing that  $x = \cos \phi$  and  $y = \sin \phi$  if  $r=1$ , **why** do you think this function is called  $d_{xy}$ ?

**Solution:**

On the  $xy$ -plane, we showed that  $d_{xy}(\theta, \phi) \sim -2 \sin 2\phi \sim \sin \phi \cos \phi \sim xy$  if  $r = 1$  (3 pts). Besides, this is a d orbital because the angular quantum number ( $l$ ) equals 2 for functions that make up  $d_{xy}$  (2 pts). This is the reason why the function is called  $d_{xy}$ .

4. The technique of finding the eigenvalues and eigenvectors of the Hamiltonian in matrix form is called “diagonalization”. You will diagonalize the Hamiltonian matrix

$$H = \begin{pmatrix} 3 & \sqrt{5}/2 \\ \sqrt{5}/2 & 1 \end{pmatrix}$$

The starting point is the equation  $H\mathbf{v} = E\mathbf{v}$  or  $(H - E\mathbf{I}) \cdot \mathbf{v} = 0$ , where  $H$  is your non-diagonal Hamiltonian matrix,  $\mathbf{I}$  is the identity matrix,  $E$  is one of the eigenvalues, and  $\mathbf{v}$  is one of the eigenvectors. In order to obtain a non-trivial solution, we need the condition  $\det ||H - E\mathbf{I}|| = 0$ .

a) **Multiply out** the determinant of the matrix  $H - E\mathbf{I}$ , to get a quadratic equation for the two eigenvalues  $E$ . **Solve** for  $E$ . This gives you the 2 eigenvalues of the  $2 \times 2$  matrix.

**Solution:**

$$\det H = \det \begin{pmatrix} 3 - E & \frac{\sqrt{5}}{2} \\ \frac{\sqrt{5}}{2} & 1 - E \end{pmatrix} = 0$$

$$(3 - E)(1 - E) - \frac{5}{4} = 0$$

$$3 + E^2 - 4E - \frac{5}{4} = 0$$

$$E^2 - 4E + 4 = \frac{9}{4}$$

$$E = 2 \pm \frac{3}{2}$$

3 pts awarded for setting  $\det = 0$ . 2 pts for two correct eigenvalues.

b) **Plug one** of these eigenvalues into the equation  $(H - IE) \cdot \mathbf{v} = 0$ , writing vector  $\mathbf{v}$  as a column vector  $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$

$$E_+ = \frac{7}{2}:$$

$$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{5}}{2} \\ \frac{\sqrt{5}}{2} & -\frac{5}{2} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

4 pts awarded for the incorrect matrix (possibly error from part a).

c) **Solve** for  $c_1$  in terms of  $c_2$  or *vice versa*, so you know your eigenvector within a constant factor.

**Solution:**

$$-\frac{1}{2}c_1 + \frac{\sqrt{5}}{2}c_2 = 0$$

$$\rightarrow c_1 = \sqrt{5}c_2$$

$$\rightarrow \mathbf{v}_+ = \begin{pmatrix} \sqrt{5}c_2 \\ c_2 \end{pmatrix}$$

Full point if set  $c_1 = 1$  then solve for  $c_2$ . 4 points for wrong sign.

d) **Normalize** the eigenvector. Remember that  $\mathbf{v}^+ \cdot \mathbf{v} = c$ , then divide by  $\sqrt{c}$  to normalize, just like for wavefunctions.

**Solution:**

Invoking the normalization condition, which states that  $\mathbf{v}^+ \cdot \mathbf{v} = c$

$$c = (\sqrt{5}c_2 \quad c_2) \begin{pmatrix} \sqrt{5}c_2 \\ c_2 \end{pmatrix} = 6c_2^2$$

Therefore, the vector corresponding to  $E_+ = \frac{7}{2}$  is

$$\mathbf{v}_+ = \frac{1}{\sqrt{6c_2^2}} \begin{pmatrix} \sqrt{5}c_2 \\ c_2 \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{5}{6}} \\ \sqrt{\frac{1}{6}} \end{pmatrix}$$

4 pts for incorrect vector (possibly from previous parts).

Similarly, the vector corresponding to  $E_- = \frac{1}{2}$  is

$$\mathbf{v}_- = \begin{pmatrix} -\sqrt{\frac{1}{6}} \\ \sqrt{\frac{5}{6}} \end{pmatrix}$$

e) **Check** that your eigenvector satisfies  $\mathbf{H}\mathbf{v} = \mathbf{E}\mathbf{v}$ . If the basis set used to calculate the Hamiltonian matrix was  $\phi_1 = \sqrt{\frac{1}{\pi}} \sin \phi$  and  $\phi_2 = \sqrt{\frac{1}{\pi}} \cos \phi$ , **what is** the wavefunction  $\psi(\phi)$  that corresponds to your eigenvector  $\mathbf{v}$ ?

**Solution:**

To check that the eigenvector satisfies  $\mathbf{H}\mathbf{v} = \mathbf{E}\mathbf{v}$ , multiply the matrix  $\mathbf{H}$  by vector  $\mathbf{v}$  and check if it is equal to  $\mathbf{E}\mathbf{v}$ .

$$H\mathbf{v}_+ = \begin{pmatrix} 3 & \frac{\sqrt{5}}{2} \\ \frac{\sqrt{5}}{2} & 1 \end{pmatrix} \begin{pmatrix} \sqrt{\frac{5}{6}} \\ \sqrt{\frac{1}{6}} \end{pmatrix} = \begin{pmatrix} \left(3 + \frac{1}{2}\right) \sqrt{\frac{5}{6}} \\ \left(\frac{5}{2} + 1\right) \sqrt{\frac{1}{6}} \end{pmatrix} = \frac{7}{2} \begin{pmatrix} \sqrt{\frac{5}{6}} \\ \sqrt{\frac{1}{6}} \end{pmatrix} = E_+ \mathbf{v}_+$$

Thus,  $\mathbf{v}_+$  satisfies the  $H\mathbf{v} = E\mathbf{v}$  equation. Similarly,  $\mathbf{v}_-$  also satisfies the equation (correct checking is worth 2 pts; incorrect checking with appreciable attempt: 1 pt; no attempt: 0 pt).

To get the wavefunctions  $\psi_+(\phi)$  and  $\psi_-(\phi)$  corresponding to  $\mathbf{v}_+$  and  $\mathbf{v}_-$ , we dot the vectors  $\mathbf{v}_+^T$  and  $\mathbf{v}_-^T$  by the vector  $\begin{pmatrix} \sqrt{\frac{1}{\pi}} \sin \phi \\ \sqrt{\frac{1}{\pi}} \cos \phi \end{pmatrix}$

$$\psi_+(\phi) = \begin{pmatrix} \sqrt{\frac{5}{6}} & \sqrt{\frac{1}{6}} \end{pmatrix} \begin{pmatrix} \sqrt{\frac{1}{\pi}} \sin \phi \\ \sqrt{\frac{1}{\pi}} \cos \phi \end{pmatrix} = \sqrt{\frac{5}{6\pi}} \sin \phi + \sqrt{\frac{1}{6\pi}} \cos \phi$$

$$\psi_-(\phi) = \begin{pmatrix} -\sqrt{\frac{1}{6}} & \sqrt{\frac{5}{6}} \end{pmatrix} \begin{pmatrix} \sqrt{\frac{1}{\pi}} \sin \phi \\ \sqrt{\frac{1}{\pi}} \cos \phi \end{pmatrix} = -\sqrt{\frac{1}{6\pi}} \sin \phi + \sqrt{\frac{5}{6\pi}} \cos \phi$$

Note that the sign is arbitrary for the above two wavefunctions, meaning you can have both positive or both negative (but not either) for the positive wavefunction. For the negative wavefunction, as long as you have opposite signs and the correct terms, your answer is acceptable. Incorrect sign: 2 pt. Using the unnormalized coefficients: 1pt.

5. (10 pts) In lecture, Gruebele started with  $\hat{A}\psi(x) = \chi(x)$ , expanded in a complete basis  $\psi(x) = \sum c_n \varphi_n(x)$  and  $\chi(x) = \sum c'_n \varphi_n$ , and showed that this is equivalent to  $A\mathbf{v} = \mathbf{u}$  or  $\sum A_{mn} c_n = c'_m$  for vectors, where  $A$  is a matrix with elements  $A_{mn} = \int dx \varphi_m^*(x) \hat{A} \varphi_n(x)$ .

Now do the same derivation in bracket notation. Start with  $\hat{A}|\psi\rangle = |\chi\rangle$ , **expand** the kets in a basis  $|n\rangle$ , and **prove** again that  $\sum A_{mn} c_n = c'_m$ , this time with  $A_{mn} = \langle m|\hat{A}|n\rangle$ .

**Solution:**

Expanding the functions  $|\psi\rangle$  and  $|\chi\rangle$  in terms of a complete orthonormal basis  $|n\rangle$ , we have

$$\hat{A} \sum_n c_n |n\rangle = \sum_n c'_n |n\rangle$$

Multiplying both sides of the equation by  $\langle m|$ , we get

$$\sum_n c_n \langle m|\hat{A}|n\rangle = \sum_n c'_n \langle m|n\rangle$$

Now, since the basis is orthonormal,  $\langle m|n\rangle = 0$  always, **except** when  $n = m$ . Thus the summation on the right vanishes, leaving only one non – zero term.

$$\sum_n c_n \langle m|\hat{A}|n\rangle = c'_m$$

or,

$$\sum_n c_n A_{mn} = c'_m$$

where,  $A_{mn} = \langle m|\hat{A}|n\rangle$ .