

Quantum Mechanics Solutions

1. **(a) (i)** If A and B are Hermitian, since $(AB)^\dagger = B^\dagger A^\dagger = BA$, operator AB is Hermitian if and only if A and B commute. So, we know that $[A, B] = 0$, which means that the Hilbert space \mathcal{H} has an orthonormal basis, call it $\{\psi_{a,b}\}$, consisting of simultaneous eigenvectors of operators A and B . That is $A\psi_{a,b} = a\psi_{a,b}$ and $B\psi_{a,b} = b\psi_{a,b}$. Since we are also given that AC is Hermitian, $[A, C] = 0$, which implies that \mathcal{H} has an orthonormal basis, call it $\{\phi_{a,c}\}$, consisting of simultaneous eigenvectors of operators A and C . If operator A has a non-degenerate spectrum, which means that there is only one eigenvector (up to a phase) that corresponds to a given eigenvalue a , this implies that the two sets of eigenvectors are equivalent; $\{\psi_{a,b}\} \equiv \{\phi_{a,c}\}$. This means that there exists a set of orthonormal basis vectors that are eigenfunctions of Hermitian operators B and C , which implies $[B, C] = 0$.

(a) (ii) Let $B|\psi_1\rangle = b_1|\psi_1\rangle$ and $B|\psi_2\rangle = b_2|\psi_2\rangle$ with $b_1 \neq b_2$, where b_1 and b_2 are real, since B is Hermitian. Since $[B, C] = 0$ and any matrix element of the zero operator is zero, we can write (using the Hermiticity of B)

$$0 = \langle \psi_1 | [B, C] | \psi_2 \rangle = \langle \psi_1 | BC | \psi_2 \rangle - \langle \psi_1 | CB | \psi_2 \rangle = \langle B\psi_1 | C | \psi_2 \rangle - \langle \psi_1 | C | B\psi_2 \rangle = (b_1 - b_2) \langle \psi_1 | C | \psi_2 \rangle$$

Since $b_1 \neq b_2$, this implies $\langle \psi_1 | C | \psi_2 \rangle = 0$.

(b) Using the suggestion, one can define the operator $C = A - iB$. The adjoint of C is $C^\dagger = A + iB$. Then,

$$C^\dagger C = A^2 + B^2 - i[A, B] = A^2 + B^2 - \alpha \Rightarrow H = C^\dagger C + \alpha$$

If $H|\psi_0\rangle = E_0|\psi_0\rangle \Rightarrow \langle \psi_0 | H | \psi_0 \rangle = E_0 \Rightarrow E_0 = \alpha + \langle \psi_0 | C^\dagger C | \psi_0 \rangle = \alpha + \langle C\psi_0 | C\psi_0 \rangle$. From the axioms of an inner product (namely, $\langle v | v \rangle \geq 0 \quad \forall |v\rangle$'s of the inner product space), we then have $E_0 \geq \alpha$. Also from the axioms of an inner product (namely, $\langle v | v \rangle = 0$ if and only if $|v\rangle = |0\rangle$ where $|0\rangle$ is the zero vector of the inner product space), if $E_0 = \alpha$, then C must annihilate the ground state, i.e. $C|\psi_0\rangle = |0\rangle$ which means $A|\psi_0\rangle = iB|\psi_0\rangle$.

2. **(a)(i)** Since the given potential is symmetric, the ground state wavefunction will also be symmetric. In the region $0 < x < a$, since the potential is zero and the ground state energy is known to vanish, the Schrödinger equation for the ground state wavefunction yields the simple result $\psi_0''(x) = 0$, which implies $\psi_0(x) = Ax + B$. Imposing the (continuity) boundary condition at $x = a$ (the wavefunction vanishes for $x > a$), we then have $\psi_0(x) = A(x - a)$. The solution for $-a < x < 0$ is obtained from symmetry of the wavefunction around the origin. Hence,

$$\psi_0(x) = A \begin{cases} x - a & 0 \leq x \leq a \\ -x - a & -a \leq x \leq 0 \end{cases}$$

Note that the continuity of the wavefunction at $x = 0$ has already been introduced from the symmetry requirement of the ground state wavefunction. We now apply the boundary condition due to the discontinuity of the derivative of the wavefunction at the position of the Dirac-delta function, namely

$$\psi'(x \rightarrow 0^+) - \psi'(x \rightarrow 0^-) = \frac{2m\Lambda}{\hbar^2} \psi(x = 0) \Rightarrow A - (-A) = \frac{2m\Lambda}{\hbar^2} (-aA) \Rightarrow \Lambda = -\frac{\hbar^2}{ma}$$

Note that Λ is negative, since the ground state energy without the Dirac-delta potential (particle in a box) would be positive, and an attractive part is needed to bring down the ground state energy eigenvalue to zero.

(a)(ii) Since the first excited state without the Dirac-delta potential vanishes at the origin (since it needs to be an odd function due to the symmetric nature of the potential), introducing a $\Lambda\delta(x)$ type of potential will have no impact on this solution (as well as all odd solutions). In other words, the original odd solutions of the Schrödinger equation without the Dirac-delta function potential still satisfy the Schrödinger equation with the Dirac-delta function potential (and the associated boundary conditions). Hence, the odd solution energy eigenvalues remain the same as the regular particle-in-a-box energy eigenvalues, which implies $E_1 = \frac{\hbar^2 \pi^2 (2)^2}{2m(2a)^2} = \frac{\hbar^2 \pi^2}{ma^2}$.

(a)(iii) The second excited state wavefunction ($n = 2$) will also be a symmetric function of x . In addition, due to the node theorem, it needs to have 2 nodes (away from the zeroes at the end points $x = \pm a$). The wavefunction should be continuous at $x = 0$, but due to the presence of the Dirac-delta potential, its first derivative should be discontinuous, i.e. the wavefunction should have a cusp at $x = 0$.

(b) For the given harmonic-oscillator-in-a-box potential, the usual “free” harmonic oscillator solutions would also satisfy the time-independent Schrödinger equation at each point x inside the box ($-a < x < a$) with the corresponding energy eigenvalues of the free oscillator. However, for an arbitrary value of the width of the box, the continuity of the wavefunction at $x = \pm a$ would not be satisfied with these free harmonic oscillator solutions in general (Since $\psi(|x| > a) = 0$, $\psi(x = \pm a)$ needs to vanish as well). On the other hand, if the positions corresponding to the outermost nodes of Hermite polynomials happen to coincide with the positions of the edges of the box, then the boundary conditions are satisfied as well. An inspection of the widths given in **(i)** and **(ii)** shows that these coincide with the zeroes of Hermite polynomials of degree $n = 2$ and $n = 3$, respectively, since $H_2(\eta) = 0 \Rightarrow \eta = \pm 1/\sqrt{2} \Rightarrow x = \pm \sqrt{\hbar/2m\omega}$, and $H_3(\eta) = 0 \Rightarrow \eta = 0, \pm\sqrt{3}/2 \Rightarrow x = 0, \pm\sqrt{3\hbar/2m\omega}$. This means that **(i)** when $a = \sqrt{\hbar/2m\omega}$, the *second excited state* solution of the free harmonic oscillator becomes the *ground state* solution of the harmonic-oscillator-in-a-box potential, which gives $E_0 = 5\hbar\omega/2$, and that **(ii)** when $a = \sqrt{3\hbar/2m\omega}$, the *third excited state* solution of the free harmonic oscillator becomes the *first excited state* solution of the harmonic-oscillator-in-a-box potential, which gives $E_1 = 7\hbar\omega/2$ in this case. Note that the two outermost nodes of the free harmonic oscillator solutions are no longer considered as nodes for the harmonic-oscillator-in-a-box problem, since they are zeroes that impose the boundary conditions at the edges. Hence, for this type of problem one gets $(n - 2)^{\text{nd}}$ excited state solution for the harmonic-oscillator-in-a-box potential coinciding with the n^{th} excited state of the free harmonic oscillator potential when the width is adjusted appropriately.

3. **(a)** From the diagonal matrix elements of H_0 , the unperturbed energy levels $E_n^{(0)}$ ($n = 1, 2, 3$) are $E_1^{(0)} = E_2^{(0)} = -1$, and $E_3^{(0)} = 0$. Since there is degeneracy in the first two unperturbed energy eigenvalues, one needs to apply degenerate perturbation theory to find the first-order corrections for these two states. The corrections are obtained by diagonalizing the perturbation matrix $b(|1\rangle\langle 2| + |2\rangle\langle 1|)$ in the degenerate subspace spanned by vectors $\{|1\rangle, |2\rangle\}$. This yields eigenvalues (first-order energy corrections) of $-b$ and b with corresponding eigenvectors (“good” zeroth-order wavefunctions) of $|\text{I}\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$ and $|\text{II}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$, respectively. For $n = 3$, standard non-degenerate perturbation theory can be applied, i.e. $E_3^{(1)} = \langle 3|H_1|3\rangle = 0$. Therefore, to first order in b , the energy eigenvalues are $E_1 = -1 - b$, $E_2 = -1 + b$, and $E_3 = 0$. The second-order energy correction for $n = 3$ can be obtained in a straightforward fashion using

$$E_3^{(2)} = \sum_{m \neq 3} \frac{|\langle m|H_1|3\rangle|^2}{E_3^{(0)} - E_m^{(0)}} = \frac{b^2}{+1} + \frac{b^2}{+1} = 2b^2$$

In finding the second-order corrections to states $|\text{I}\rangle$ and $|\text{II}\rangle$, we exclude the sum over both states, i.e.

$$E_{\text{I}}^{(2)} = \sum_{m \neq \text{I, II}} \frac{|\langle m|H_1|\text{I}\rangle|^2}{E_{\text{I}}^{(0)} - E_m^{(0)}} = \frac{|\langle 3|H_1|\text{I}\rangle|^2}{E_{\text{I}}^{(0)} - E_3^{(0)}} = \frac{\frac{1}{2}|\langle 3|H_1|1\rangle - \langle 3|H_1|2\rangle|^2}{-1 - 0} = \frac{\frac{1}{2}|b - b|^2}{-1} = 0$$

$$E_{\text{II}}^{(2)} = \sum_{m \neq \text{I, II}} \frac{|\langle m|H_1|\text{II}\rangle|^2}{E_{\text{II}}^{(0)} - E_m^{(0)}} = \frac{|\langle 3|H_1|\text{II}\rangle|^2}{E_{\text{II}}^{(0)} - E_3^{(0)}} = \frac{\frac{1}{2}|\langle 3|H_1|1\rangle + \langle 3|H_1|2\rangle|^2}{-1 - 0} = \frac{\frac{1}{2}|b + b|^2}{-1} = -2b^2$$

Therefore, to second order in b , the energy eigenvalues are $E_1 = -1 - b$, $E_2 = -1 + b - 2b^2$, and $E_3 = 2b^2$.

(b) Since the lowest zeroth-order energy eigenvalue of -1 corresponds to eigenstate $|1\rangle$, we write the first-order correction $|\psi_1^{(1)}\rangle$ to the ground state wavefunction as

$$|\psi_1^{(1)}\rangle = \sum_{m \neq 1} \frac{\langle m|H_1|1\rangle|m\rangle}{E_1^{(0)} - E_m^{(0)}} = \frac{b}{-1 - 0}|2\rangle + \frac{2b}{-1 - 1}|3\rangle = -b(|2\rangle + |3\rangle).$$

Therefore, the (unnormalized) ground state wavefunction up to first-order is $|\psi_1\rangle = |1\rangle - b|2\rangle - b|3\rangle \equiv |\chi\rangle$. Using this as a trial wavefunction, one needs to compute $\frac{\langle \chi|H|\chi\rangle}{\langle \chi|\chi\rangle}$, which gives an upper bound for the ground state energy E_1 . Carrying out the calculations one finds $E_1 \leq \frac{-1 - 5b^2}{1 + 2b^2}$. Keeping terms up to b^2 , this yields $E_1 \leq -1 - 3b^2$. Perturbative ground state energy up to second order yields

$$E_1 = E_1^{(0)} + \langle 1|H_1|1\rangle + \sum_{m \neq 1} \frac{|\langle m|H_1|1\rangle|^2}{E_1^{(0)} - E_m^{(0)}} = -1 + 0 + \frac{b^2}{-1 - 0} + \frac{(2b)^2}{-1 - 1} = -1 - 3b^2$$

which coincides with the upper bound estimate obtained from the variational treatment.

4. (a) Energy measurement: Bound state energy eigenvalues for the hydrogen atom are given as $E_n = -\frac{13.6 \text{ eV}}{n^2}$, where n is the principal quantum number. Since the given (normalized) $\psi(\mathbf{r})$ has already been expanded as a linear combination of Hamiltonian eigenstates, the possible outcomes and the corresponding probabilities (the modulus square of the expansion coefficients) of energy measurements can be written down straightforwardly. The possible outcomes are -13.6 , -3.4 , -1.51 , 0.85 , and -0.544 eV with probabilities of $\frac{3}{32}$, $\frac{1}{4}$, $\frac{3}{16}$, $\frac{3}{8}$, and $\frac{3}{32}$, respectively.

L^2 measurement: The $\phi_{n\ell m}$ states that appear in the expansion of $\psi(\mathbf{r})$ are also L^2 eigenstates with eigenvalues of $\ell(\ell+1)\hbar^2$. Therefore, the possible outcomes from L^2 measurements on $\psi(\mathbf{r})$ are $6\hbar^2$, $2\hbar^2$, and 0 with corresponding probabilities of $\frac{6+12+3}{32} = \frac{21}{32}$, $\frac{1}{4}$, and $\frac{3}{32}$, respectively.

Π measurement: The parity of $\phi_{n\ell m}$ eigenstates of the hydrogen atom is $(-1)^\ell$ (due to the parity of the spherical harmonics $Y_{\ell m}$). Therefore, the possible outcomes from Π measurements on $\psi(\mathbf{r})$ are $+1$ and -1 with probabilities of $\frac{6+12+3+3}{32} = \frac{3}{4}$ and $\frac{1}{4}$, respectively.

- (b) The uncertainty $(\Delta L_z)_\psi$ of L_z in the state $\psi(\mathbf{r})$ can be computed using the standard expression for the uncertainty, the expansion coefficients $c_{n\ell m}$ that appear in the expansion of $\psi(\mathbf{r})$ in terms of $\phi_{n\ell m}$, and noticing that $\phi_{n\ell m}$ is an L_z eigenstate with eigenvalue $m\hbar$:

$$(\Delta L_z)_\psi = \sqrt{\langle L_z^2 \rangle - \langle L_z \rangle^2} = \left[\sum_m |c_{n\ell m}|^2 m^2 \hbar^2 - \left(\sum_m |c_{n\ell m}|^2 m \hbar \right)^2 \right]^{1/2} = \frac{\sqrt{327}}{16} \hbar.$$

- (c) If L^2 measurement yields the largest possible value ($6\hbar^2$), the state of the system immediately after the measurement can be written down (using the measurement postulate) by retaining only the L^2 eigenstates with $6\hbar^2$ eigenvalue that appear in the expansion of the state before the L^2 measurement (keeping the same ratio of coefficients), i.e.

$$\psi_{\text{after}}(\mathbf{r}) \propto \frac{\sqrt{3}}{4} \phi_{321}(\mathbf{r}) - \frac{i\sqrt{3}}{2\sqrt{2}} \phi_{42-2}(\mathbf{r}) + \frac{\sqrt{3}}{4\sqrt{2}} \phi_{520}(\mathbf{r}).$$

Normalizing this, one gets $\psi_{\text{after}}(\mathbf{r}) = \sqrt{\frac{2}{7}} \phi_{321}(\mathbf{r}) - \frac{2i}{\sqrt{7}} \phi_{42-2}(\mathbf{r}) + \frac{1}{\sqrt{7}} \phi_{520}(\mathbf{r})$. Therefore, the possible outcomes from an L_z measurement are $+\hbar$, $-2\hbar$, and 0 with probabilities of $\frac{2}{7}$, $\frac{4}{7}$, and $\frac{1}{7}$, respectively. Notice that since L_z commutes with the Hamiltonian (which governs the time evolution of the system), these probabilities are independent of time (In other words, time evolution of the system only modifies each $c_{n\ell m}$ coefficient right after the L^2 measurement by a pure phase, but leaves $|c_{n\ell m}|^2$ invariant).

- (d) The energy measurement in which the highest possible value (-0.544 eV) is obtained collapses the state of the system to $\phi_{520}(\mathbf{r})$. Writing $\phi_{520}(\mathbf{r}) = R_{52}(r)Y_{20}(\Omega)$. Taking the modulus square of this and integrating over the solid angle yields $P(r) = 4\pi r^2 |R_{52}(r)|^2$. The radial wavefunction $R_{n\ell}$ has $n - \ell - 1$ radial nodes (away from $r = 0$). Therefore, the sketch of $P(r)$ should show a curve that starts from 0 at $r = 0$ and has 2 nodes (or 3 local maxima growing in magnitude as r gets larger) and exponentially decaying as $r \rightarrow \infty$ after the third (global) maximum. The asymptotic behavior of $R_{n\ell}(r \rightarrow 0) \sim r^\ell$. Therefore, $P(r \rightarrow 0) \sim r^2(r^2)^2 \sim r^6$.

- (e) The energy measurement in which the lowest possible value (-13.6 eV) is obtained collapses the state of the system to $\phi_{100}(\mathbf{r})$, i.e. the $1s$ ground state of the hydrogen atom. The radial wavefunction $R_{10}(r) \sim e^{-r/a_0}$ where $a_0 = 0.529 \text{ \AA}$ is the Bohr radius. The radial wavefunction is finite (achieving its maximum) at the origin, since it asymptotically behaves as $r^0 = \text{constant}$ near the origin, and exponentially decays (no nodes) as $r \rightarrow \infty$. The radial probability distribution $P(r) \sim r^2 e^{-2r/a_0}$ starts from 0 at $r = 0$ and has one global maximum at $r = a_0$ and decays exponentially.

5. **(a)** With the edges of the potential well placed at $x = 0$ and $x = a$, the normalized single-particle energy eigenstates are $\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ with corresponding eigenvalues of $E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$.

Ground State: If we put both electrons in the single-particle ground state ($n_1 = n_2 = 1$), we can only form a symmetric spatial part. This is OK, since we can ensure the anti-symmetric nature of the overall wavefunction by choosing an anti-symmetric spin part. For 2 electrons, this means the singlet state.

$$\Psi_0(x_1, s_1; x_2, s_2) = \phi_1(x_1)\phi_1(x_2) \otimes \frac{1}{\sqrt{2}} \left(|+\rangle|-\rangle - |-\rangle|+\rangle \right)$$

The ground state is non-degenerate with an energy of $\frac{\hbar^2 \pi^2}{2ma^2} + \frac{\hbar^2 \pi^2}{2ma^2} = \frac{\hbar^2 \pi^2}{ma^2}$.

First Excited State: We can place one of the electrons in $n = 2$ while keeping the other one in $n = 1$. We can form either a symmetric or anti-symmetric spatial part in doing so. To ensure the anti-symmetric nature of the overall wavefunction we can combine the symmetric spatial part with an anti-symmetric spin part (singlet) or the anti-symmetric spatial part with the symmetric spin part (triplet).

$$\begin{aligned} \Psi_1(x_1, s_1; x_2, s_2) &= \frac{1}{\sqrt{2}} \left(\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1) \right) \otimes \frac{1}{\sqrt{2}} \left(|+\rangle|-\rangle - |-\rangle|+\rangle \right) \text{ or} \\ &= \frac{1}{\sqrt{2}} \left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1) \right) \otimes \frac{1}{\sqrt{2}} \left(|+\rangle|-\rangle + |-\rangle|+\rangle \right) \text{ or} \\ &= \frac{1}{\sqrt{2}} \left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1) \right) \otimes |+\rangle|+\rangle \text{ or} \\ &= \frac{1}{\sqrt{2}} \left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1) \right) \otimes |-\rangle|-\rangle \end{aligned}$$

Therefore, the first excited state is 4-fold degenerate with an energy of $\frac{\hbar^2 \pi^2}{2ma^2} + \frac{\hbar^2 \pi^2 (2)^2}{2ma^2} = \frac{5\hbar^2 \pi^2}{2ma^2}$.

Second Excited State: Since $1^2 + 3^2 > 2^2 + 2^2$, the second excited state is obtained by placing both electrons in the $n = 2$ single-particle state. As in the ground state case, we can only form a symmetric spatial part with $n_1 = n_2 = 2$, which means that the spin part can only be the singlet state.

$$\Psi_2(x_1, s_1; x_2, s_2) = \phi_2(x_1)\phi_2(x_2) \otimes \frac{1}{\sqrt{2}} \left(|+\rangle|-\rangle - |-\rangle|+\rangle \right)$$

The second excited state is non-degenerate with an energy of $\frac{\hbar^2 \pi^2 (2)^2}{2ma^2} + \frac{\hbar^2 \pi^2 (2)^2}{2ma^2} = \frac{4\hbar^2 \pi^2}{ma^2}$.

(b) Placing \vec{A} along the z -axis and denoting $|\vec{A}| = A$, the Hamiltonian becomes $H = A(S_{1z} - S_{2z})$, which will be diagonal when represented in the uncoupled $|m_1\rangle|m_2\rangle$ basis with eigenvalues of $A(m_1 - m_2)\hbar$. The initial state of the system is one in which the total spin of the system is zero, i.e. the $|S = 0, M = 0\rangle$ state in the coupled representation. In order to write down the time evolution of the state in a straightforward way, it is best to express the initial state in terms of the Hamiltonian eigenstates (i.e. the uncoupled basis vectors in this case). From the information provided (expansion of $|2, 0\rangle$ and $|1, 0\rangle$ in terms of uncoupled basis vectors), we can obtain the expansion of the $|0, 0\rangle$ coupled state using the orthonormality of the $|S, M\rangle$ states. Writing $|0, 0\rangle = \alpha|+\rangle|-\rangle + \beta|0\rangle|0\rangle + \gamma|-\rangle|+\rangle$ and using $\langle 0, 0|2, 0\rangle = \langle 0, 0|1, 0\rangle = 0$ and $\alpha^2 + \beta^2 + \gamma^2 = 1$ (Clebsch-Gordan coefficients can be chosen to be real), one arrives at $|0, 0\rangle = \frac{1}{\sqrt{3}}(|+\rangle|-\rangle - |0\rangle|0\rangle + |-\rangle|+\rangle)$. The time-evolved state can then be written using eigenvalues $2A\hbar$, 0 , and $-2A\hbar$ for states $|+\rangle|-\rangle$, $|0\rangle|0\rangle$, and $|-\rangle|+\rangle$, respectively, as

$$|\Psi(t)\rangle = \frac{1}{\sqrt{3}} \left(|+\rangle|-\rangle e^{-i2At} - |0\rangle|0\rangle + |-\rangle|+\rangle e^{i2At} \right)$$

The first time $|\Psi(t)\rangle$ becomes orthogonal to $|\Psi(0)\rangle$ can be found by setting $\langle \Psi(0)|\Psi(t)\rangle = 0$ which yields $e^{-i2At} + 1 + e^{i2At} = 0 \Rightarrow \cos(2At) = -\frac{1}{2} \Rightarrow t = \frac{\pi}{3A}$.