Solution to final exam FY2045 Quantum Mechanics I December 14th, 2024

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Problem 1 Multiple choice problems

a) The general rule when adding two spins is that the total spin quantum number can take the values

$$s = s_1 + s_2, s_1 + s_2 - 1, \dots |s_1 - s_2|.$$

When adding more than two spins, we have to repeat this procedure. For $\frac{1}{2} + \frac{1}{2}$ we get

$$s = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} - \frac{1}{2} = 1, 0$$

For $\frac{1}{2} + \frac{1}{2} + 1$,

$$s = 1 + 1, 1 - 1, 0 + 1 \implies s = 2, 1, 0,$$

Hence, alternative \mathbf{E} is the correct one.

b) The relevant eigenvalue equation is $S_y|\chi_y^-\rangle = \frac{\hbar}{2}\sigma_y|\chi_y^-\rangle = -\frac{\hbar}{2}|\chi_y^-\rangle$. By using the Pauli matrix σ_y , one can see that alternative **E** is the correct one.

c) The dual vector of $|n\rangle$ is $\langle n|$. For a general vector $|\psi\rangle = \sum_n c_n |n\rangle$, the dual vector is given by $\langle \psi | = \sum_n c_n^* \langle n |$. In this case we therefore get

$$\langle \psi | = A^* \lfloor (-3i) \langle 1 | + (1+2i) \langle 2 | + \langle 3 | \rfloor.$$
 (1)

This is option \mathbf{D} .

d) We require

$$1 = \langle \psi | \psi \rangle = |A|^2 [\langle 1| - 2i\langle 2| + 2\langle 3|] [|1\rangle + 2i|2\rangle + 2|3\rangle] = |A|^2 [1 + 4 + 4] = 9|A|^2.$$
(2)

Choosing A real and positive, we get $A = \frac{1}{3}$ — option C is correct.

e) The probabilities associated with each energy is $P_n = |c_n|^2$, where $c_1 = A$, $c_2 = -2i$ and $c_3 = 2A$. Hence,

$$\langle E \rangle_{\psi} = |A|^2 [E_1 + 4E_2 + 4E_3] = \frac{1}{9} \cdot \frac{3}{2} \hbar \omega + \frac{4}{9} \cdot \frac{5}{2} \hbar \omega + \frac{4}{9} \cdot \frac{7}{2} \hbar \omega = \frac{17}{6} \hbar \omega.$$
(3)

Option \mathbf{E} is the correct answer.

f) Let us go through the wrong options first. Option **B**: The integral of the probability density has to yield 1, not the probability density itself. Option **D**: The time-dependent wave function after the measuring E_1 is $\Psi(x,t) = \psi_1(x)e^{-iE_1t\hbar}$. Option **E**: The ratio of the probabilities for measuring E_1 or E_2 is $(\frac{C_1}{C_1})^2$. Hence, we are left with the probability density (options **A** and **C**) which oscillates with time before the measurement is made

$$|\Psi(x,t)|^2 = |\psi_1(x)|^2 + |\psi_2(x)|^2 + 2C_1C_2\psi_1(x)\psi_2(x)\cos\left(\frac{E_1 - E_2}{\hbar}t\right).$$
(4)

Hence, **A** is the correct option.

g) Firstly, one can measure any of the spin components, therefore option **E** is wrong. Secondly, if the probability for measuring S_z "up" is $\frac{2}{5}$ (option **A**) this leads immediately to the probability S_z "down" for $1 - \frac{2}{5} = \frac{3}{5}$ (option **B**). This leads to a contradiction because we can have only one correct answer (and neither of them is correct anyhow). Testing the eigenspinors for S_x and S_y

χ⁺_x = 1/√2 (1) [This one has to deduce because it was not listed in Problem 1b).]
 χ⁺_y = 1/√2 (1)/i

for the probability amplitude $\langle \chi_{x,y}^+ | \chi \rangle$ shows that option **C** is the correct answer.

h) Normalization of the wave function in the momentum space leads to a simple integral and $C = \frac{1}{\sqrt{p_0}}$. The expectation value $\langle \phi(p) | p^2 | \phi(p) \rangle$ is also another simple integral with the outcome $\langle p^2 \rangle = \frac{p_0^2}{3}$. Therefore, option **A** is the correct answer.

i) Let us first check the energy levels, which are $E_n = (n_x^2 + n_y^2)\epsilon$. This means that the eigenstates ψ_{11} and ψ_{22} correspond to energies $E_{11} = 2\epsilon$ and $E_{22} = 8\epsilon$. The eigenstates ψ_{12} and ψ_{21} are degenerate with energy $E = 5\epsilon$. Therefore, the options **C**, **D** and **E** are wrong. A measurement of the degenerate energy $E_{12} = E_{21} = 5\epsilon$ leads to a (normalized) linear combination the degenerate eigenstates $\Psi = \frac{1}{\sqrt{2}}(\psi_{12} + i\psi_{21})$ with the probability $\frac{1}{5} + \frac{1}{5} = \frac{2}{5}$. Hence, the option **B** is correct.

j) Since the particles are fermions, they cannot all be in the same single-particle state. However, two particles can occupy each single-particle energy state due to the two possible spin directions. Hence, to minimize the total system energy we shall need to test (partly) filling the four lowest energy states, which have quantum numbers (0, 0, 0), (1, 0, 0), (0, 1, 0)and (0, 0, 1). Note that $n_{x/y/z}$ indices start running from 0 unlike in the case of an infinite quantum well. Let us go through the three lowest energy configurations (n_x, n_y, n_z) :

(i) Configuration $2 \times (0,0,0) + 2 \times (1,0,0) + 1 \times (0,1,0) \rightarrow E = 19\hbar\omega$

(ii) Configuration $2 \times (0,0,0) + 1 \times (1,0,0) + 2 \times (0,1,0) \to E = 20\hbar\omega$

(iii) Configuration $2 \times (0,0,0) + 2 \times (1,0,0) + 1 \times (0,0,1) \to E = 20\hbar\omega$

Hence, \mathbf{C} is the correct answer.

Problem 2 Short answer questions

a) The ladder operators of harmonic oscillatorare defined as

$$\begin{split} a &= \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + \frac{i}{\sqrt{2m\hbar\omega}} \hat{p} \\ a^{\dagger} &= \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - \frac{i}{\sqrt{2m\hbar\omega}} \hat{p}. \end{split}$$

This shows that they are the adjoints of each other, not themselves as required for Hermitian operators, and therefore, they will not produce real eigenvalues. The ladder operators shift energy eigenstates up or down rather than providing measurable observables directly. On the other hand, their product $N = a^{\dagger}a$ (number operator) and Hamiltonian are Hermitian.

b) The short answer is, yes. Since $\langle H \rangle_{\psi} \geq E_0$, the variational method turns the estimation of the ground state energy into a minimization problem. By using trial functions (states) ψ $(|\psi\rangle)$ with many free parameters, it is possible to achieve very good estimates for the ground state of a system. Similarly, the variational method can be applied to excited states provided that the trial wave function is kept orthogonal to any lower lying states. This means adding corresponding constraints in the minimization problem. In practice, the causes increased complexity as one moves higher up in the excited states.

c) The hyperfine structure of the hydrogen atom arises due to the interaction between the magnetic moment of the electron and the magnetic moment of the nucleus (proton). It is a finer splitting of spectral lines than the fine structure, caused by these magnetic interactions. For the ground state, the interaction is characterized by the dot product $\hat{S}_e \cdot \hat{S}_p$ between the individual spins.

d) A coherent state in the context of a quantum harmonic oscillator is a special type of quantum state that exhibits properties closely resembling those of a classical harmonic oscillator. It is defined as an eigenstate of the annihilation operator

$$a|\alpha\rangle = \alpha |\alpha\rangle$$

Coherent states minimize the Heisenberg uncertainty relation $\Delta x \Delta p = \frac{\hbar}{2}$, and have equal uncertainties in position and momentum.

Problem 3 Angular momentum addition

a) The total number of coupled angular momentum states is given by $(2j_1 + 1)(2j_2 + 1)$ where $j_1 = \frac{3}{2}$ and $j_1 = \frac{1}{2}$. There are 8 angular momentum configurations $|j_1, m_1\rangle|j_2, m_2\rangle$ for the coupled system.

b) The total angular momentum values are given by $j = |j_1 - j_2|, ..., j_1 + j_2$. This means that there are two possible values j = 1 or j = 2. For each, $m_j = -j, ..., j$. Thus, there are 3 possible m_j values (-1,0,+1) for j = 1 and 5 possible m_j values (-2,-1,0,+1,+2) for j = 2. The combinations of these yield 8 angular momentum configuration $|j,m\rangle$ which is in agreement with a).

c) Let use recall that $J_z = J_{1z} + J_{2z}$ which means that it operates on the state $|j_1 j_2 m_1 m_2\rangle$ in the following manner

$$J_z |j_1 j_2 m_1 m_2\rangle = \hbar (m_1 + m_2) |j_1 j_2 m_1 m_2\rangle.$$
(5)

Let us operate next with the commutator $[J_z, J_{1+}] = J_z J_{1+} - J_{1+} J_z$

$$J_z J_{1+} |j_1 j_2 m_1 m_2\rangle = J_z \hbar \sqrt{(j_1 - m_1)(j_1 + m_1 + 1)} |j_1 j_2 m_1 + 1 m_2\rangle$$
(6)

$$=\hbar^2(m_1+m_2+1)\sqrt{(j_1-m_1)(j_1+m_1+1)}|j_1j_2m_1+1m_2\rangle, \quad (7)$$

$$J_{1+}J_z|j_1j_2m_1m_2\rangle = J_{1+}\hbar(m_1+m_2)|j_1j_2m_1m_2\rangle$$
(8)

$$=\hbar^2(m_1+m_2)\sqrt{(j_1-m_1)(j_1+m_1+1)}|j_1j_2m_1+1m_2\rangle.$$
(9)

This lead to the result

$$[J_z, J_{1+}]|j_1 j_2 m_1 m_2\rangle = \hbar J_{1+}|j_1 j_2 m_1 m_2\rangle, \tag{10}$$

and we can conclude that $[J_z, J_{1+}] = \hbar J_{1+}$.

d) Let us write $\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2$. We can now expand the commutator as

$$[\hat{\mathbf{J}}^2, J_{1+}] = [\hat{\mathbf{J}}^2_1, J_{1+}] + [\hat{\mathbf{J}}^2_2, J_{1+}] + 2[\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2, J_{1+}].$$
(11)

The first commutator gives zero because $\hat{\mathbf{J}}_1^2$ is a scalar operator and does not involve m_1 . The second one involves operations on different subsystem and gives zero as well. We are left with the last one

$$[\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2, J_{1+}] = \hat{\mathbf{J}}_1 \cdot [\hat{\mathbf{J}}_2, J_{1+}] + [\hat{\mathbf{J}}_1, J_{1+}] \cdot \hat{\mathbf{J}}_2 = [\hat{\mathbf{J}}_1, J_{1+}] \cdot \hat{\mathbf{J}}_2,$$
(12)

where we have to use the component form of the ladder operator $\mathbf{J}_1 = J_{1x} + iJ_{1y}$ next. By using the standard commutator rules for the components, one can show that

$$[\mathbf{\tilde{J}}_1, J_{1+}] \cdot \mathbf{\tilde{J}}_2 = [J_{1x}, J_{1+}]J_{2x} + [J_{1y}, J_{1+}]J_{2y} + [J_{1z}, J_{1+}]J_{2z}$$
(13)

$$= [J_{1x}, iJ_{1y}]J_{2x} + [J_{1y}, J_{1x}]J_{2y} + [J_{1z}, J_{1+}]J_{2z}$$
(14)

$$= -\hbar J_{1z}J_{2x} - i\hbar J_{1z}J_{2y} + \hbar J_{1+}J_{2z}.$$
 (15)

Therefore, the final result is

$$[\hat{\mathbf{J}}^2, J_{1+}] = 2[\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2, J_{1+}] = 2\hbar J_{1z}(-J_{2x} - iJ_{2y}) + 2\hbar J_{1+}J_{2z}$$
(16)

$$= -2\hbar J_{1z}J_{2+} + 2\hbar J_{1+}J_{2z}.$$
 (17)

This result may seem confusing at first but it highlights the fact that $\hat{\mathbf{J}}^2$ couples $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$. Further, it operates on the "new states", that is the quantum numbers j and m_j , while the latter are associated with the "old states" of the individual particles.

e) The state with the highest total angular momentum $j_{\text{max}} = 2$ and $m_j = j_{\text{max}} = 2$ corresponds to the case where the individual spins are aligned "up" and $m_j = m_1 + m_2$. Therefore, there is a direct correspondence $|2, 2\rangle_J = |\frac{3}{2}, \frac{1}{2}\rangle_S$.

f) Since, $m_j = j_{\text{max}} - 1 = 1$ we will need to solve the state $|2,1\rangle_J$ by using the ladder operator

$$\hat{J}_{-}|j,m\rangle = \sqrt{(j+m)(j-m+1)}|j,m\pm 1\rangle$$
(18)

on the highest total angular momentum state (as stated above). We will do this with respect to the "new" and "old" states

$$\hat{J}_{-}|2,2\rangle_{J} = \sqrt{(2+2)(2-2+1)}|2,1\rangle_{J} = 2\hbar|2,1\rangle_{J}$$
(19)

$$(\hat{J}_{1-} + \hat{J}_{2-})|\frac{3}{2}, \frac{1}{2}\rangle_S = \hbar \sqrt{(\frac{3}{2} + \frac{3}{2})(\frac{3}{2} - \frac{3}{2} + 1)}|\frac{1}{2}, \frac{1}{2}\rangle_S$$
(20)

$$+\hbar\sqrt{(\frac{1}{2}+\frac{1}{2})(\frac{1}{2}-\frac{1}{2}+1)|\frac{3}{2},-\frac{1}{2}\rangle_{S}}$$
(21)

$$=\sqrt{3}\hbar|\frac{1}{2},\frac{1}{2}\rangle_{S} + \hbar|\frac{3}{2},-\frac{1}{2}\rangle_{S}$$
(22)

There is equivalence between the two equations and we can write

$$|2,1\rangle_J = \frac{\sqrt{3}}{2}|\frac{1}{2},\frac{1}{2}\rangle_S + \frac{1}{2}|\frac{3}{2},-\frac{1}{2}\rangle_S.$$
(23)

A quick check of the coefficients reveals that the new state is normalized, as it should.

g) Repeat the procedure for $m_j = j_{\text{max}} - 2 = 0$ corresponding to the state $|2,0\rangle_J$ by using the ladder operator to the previous result for $|2,1\rangle_J$.

$$\hat{J}_{-}|2,1\rangle_{J} = \sqrt{(2+1)(2-1+1)}|2,0\rangle_{J} = \sqrt{6}\hbar|2,0\rangle_{J}$$
(24)

$$(J_{1-} + J_{2-})|\frac{1}{2}, \frac{1}{2}\rangle_S = 2\hbar |-\frac{1}{2}, \frac{1}{2}\rangle_S + \hbar |\frac{1}{2}, -\frac{1}{2}\rangle_S$$
(25)

$$(\hat{J}_{1-} + \hat{J}_{2-})|_{2}^{3}, -\frac{1}{2}\rangle_{S} = \sqrt{3}\hbar|-\frac{1}{2}, -\frac{1}{2}\rangle_{S}$$
(26)

Note that the ladder operator \hat{J}_{2-} cannot operate on the state $|\frac{3}{1}, -\frac{1}{2}\rangle_S$ because it corresponds to $m_2 = m_{2\min}$. The equivalence between the new and old states leads to the final result.

$$|2,0\rangle_J = \frac{1}{\sqrt{2}}|-\frac{1}{2},\frac{1}{2}\rangle_S + \frac{1}{\sqrt{2}}|\frac{1}{2},-\frac{1}{2}\rangle_S,$$
(27)

which is normalized.

h) The state with a reduced total angular momentum $j = j_{\text{max}} - 1 = 1$ and $m_j = j_{\text{max}} - 1 = 1$ corresponds to a new set of ladders for the angular momentum configurations. Therefore, the ladder operator method is not the solution this time. Instead, we require that the state $|1,1\rangle_J$ has to be orthonormal with respect to the state $|2,1\rangle_J$. For $m_j = m_1 + m_2 = 1$, the only possible old states contributing are $|\frac{3}{2}, -\frac{1}{2}\rangle_S$ and $|\frac{1}{2}, \frac{1}{2}\rangle_S$ leading to

$$|1,1\rangle_J = A|\frac{3}{2}, -\frac{1}{2}\rangle_S + B|\frac{1}{2}, \frac{1}{2}\rangle_S,$$
 (28)

where we need to solve the cofactors such that $\langle 2, 1|1, 1\rangle_J = 0$. Combining this with the normalization leads to the result

$$|1,1\rangle_J = -\frac{\sqrt{3}}{2}|\frac{3}{2}, -\frac{1}{2}\rangle_S + \frac{1}{2}|\frac{1}{2}, \frac{1}{2}\rangle_S.$$
⁽²⁹⁾

We have solved now 4 of the 8 coupled angular momentum states. The remaining states would follow by applying the ladder operators subsequently. Of course, one can use tables for the Clebsch-Gordan coefficients which we have been calculating herein.

Problem 4 Identical particles - two boson

a) We shall solve the wave functions and total energies of an unperturbed system. Recall that the potential for a one-dimension infinite well is

$$V(x) = \begin{cases} 0, & 0 \le x \le L, \\ \infty, & \text{otherwise} \end{cases}$$
(30)

and one can find the related wavefunctions and energies in the formula sheet. For two bosons, the eigenstate and eigenenergies of the ground state (n = 1) are

$$\Psi_{\text{ground}}(x_1, x_2) = \frac{2}{L} \sin\left(\frac{\pi x_1}{L}\right) \sin\left(\frac{\pi x_2}{L}\right)$$
(31)

and

$$E_{\text{ground}} = 2E_1 = 2\frac{\pi^2\hbar^2}{2mL^2} = \frac{\pi^2\hbar^2}{mL^2}.$$
 (32)

By taking into account the symmetry requirement for bosons (symmetry upon particle exchange), the first excited state $(n_1 = 1, n_2 = 2)$ becomes,

$$\Psi_{\text{excited}}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2) \right].$$
(33)

Substitution of the single-particle eigenfunctions results in

$$\Psi_{\text{excited}}(x_1, x_2) = \frac{2}{L\sqrt{2}} \left[\sin\left(\frac{\pi x_1}{L}\right) \sin\left(\frac{2\pi x_2}{L}\right) + \sin\left(\frac{2\pi x_1}{L}\right) \sin\left(\frac{\pi x_2}{L}\right) \right].$$
(34)

The corresponding total energy is

$$E_{\text{excited}} = E_1 + E_2 = \frac{\pi^2 \hbar^2}{2mL^2} + \frac{4\pi^2 \hbar^2}{2mL^2} = \frac{5\pi^2 \hbar^2}{2mL^2}.$$
 (35)

b) Let us start from the probability density. If we already take into account the action of the δ -function in the double integral (for x_1 and x_2), the wave function (for a single integral $x = x_1 = x_2$) becomes

$$\Psi_{\text{ground}}(x,x) = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$$
(36)

The probability density is thus

$$|\Psi_{\text{ground}}(x,x)|^2 = \left(\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)\right)^2 = \frac{4}{L^2} \cdot \sin^4\left(\frac{\pi x}{L}\right)$$
(37)

Energy correction due to the ground state perturbation is

$$E_{\rm corr} = \langle \Psi_{\rm ground} | V | \Psi_{\rm ground} \rangle = -V_0 \frac{4}{L} \int_0^L \sin^4\left(\frac{\pi x}{L}\right) dx \tag{38}$$

where using the trigonometric equation

$$\sin^4(a) = \frac{3}{8} - \frac{1}{2}\cos(2a) + \frac{1}{8}\cos(4a) \tag{39}$$

the integral becomes

$$E_{\rm corr} = -V_0 \frac{4}{L} \int_0^L \left(\frac{3}{8} - \frac{1}{2}\cos\left(\frac{2\pi x}{L}\right) + \frac{1}{8}\cos\left(\frac{4\pi x}{L}\right)\right) dx.$$
 (40)

The two latter terms contribute to zero once integrated over the full range of the finite potential (symmetry!). We are left with the first integral

$$\int_{0}^{L} \frac{3}{8} dx = \frac{3}{8}L \tag{41}$$

which is trivial. Therefore,

$$E_{\rm corr} = -V_0 \frac{4}{L} \cdot \frac{3}{8} L = -\frac{3}{2} V_0 \tag{42}$$

and the ground state energy becomes

$$E_{\text{ground}} = \frac{\pi^2 \hbar^2}{mL^2} - \frac{3}{2} V_0.$$
(43)

c) The first-order energy correction to the first excited state is given by:

$$E_{\rm corr} = \langle \Psi_{\rm excited} | V_{\rm int} | \Psi_{\rm excited} \rangle \tag{44}$$

$$= -V_0 L \int_0^L \int_0^L \Psi_{\text{excited}}^*(x_1, x_2) \delta(x_1 - x_2) \Psi_{\text{excited}}(x_1, x_2) \, dx_1 \, dx_2.$$
(45)

Using the delta function $\delta(x_1 - x_2)$, again, this simplifies to:

$$E_{\rm corr} = -V_0 L \int_0^L |\Psi_{\rm excited}(x, x)|^2 \, dx.$$
(46)

The wave function at $x_1 = x_2 = x$ becomes

$$\Psi_{\text{excited}}(x,x) = \frac{1}{\sqrt{2}} \Big(\psi_1(x)\psi_2(x) + \psi_2(x)\psi_1(x) \Big) = 2 \cdot \frac{1}{\sqrt{2}} \frac{2}{L} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right), \quad (47)$$

and the corresponding probability density is

$$|\Psi_{\text{excited}}(x,x)|^2 = \left(\frac{2\sqrt{2}}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\right)^2 = \frac{8}{L^2}\sin^2\left(\frac{\pi x}{L}\right)\sin^2\left(\frac{2\pi x}{L}\right).$$
 (48)

Next, we substitute this in the energy correction

$$E_{\rm corr} = -\frac{8V_0}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) \sin^2\left(\frac{2\pi x}{L}\right) \, dx. \tag{49}$$

Using the trigonometric identity

$$\sin^2 \theta_1 \sin^2 \theta_2 = \frac{1}{4} \Big[1 - \cos(2\theta_1) - \cos(2\theta_2) + \cos(2\theta_1 - 2\theta_2) \Big], \tag{50}$$

we expand the integral further.

$$E_{\rm corr} = -\frac{8V_0}{L} \cdot \frac{1}{4} \int_0^L \left[1 - \cos\left(\frac{2\pi x}{L}\right) - \cos\left(\frac{4\pi x}{L}\right) + \cos\left(\frac{2\pi x}{L}\right)\right] dx \tag{51}$$

$$= -\frac{2V_0}{L} \int_0^L \left[1 - \cos\left(\frac{4\pi x}{L}\right)\right] dx.$$
(52)

Again, the latter integral contributes zero and we are left with

$$E_{\rm corr} = -\frac{2V_0}{L} \int_0^L 1 \, dx = -\frac{2V_0}{L} \cdot L = -2V_0.$$
 (53)

Therefore, the total energy of the first excited state is

$$E_{\text{excited}} = \frac{5\pi^2 \hbar^2}{mL^2} - 2V_0.$$
 (54)

Comparing the ground state and the first excited state before and after perturbation reveals that, in addition to lowering the total energies in both cases, V reduces the energy gap by an amount $\frac{1}{2}V_0$.

Problem 5 Variational principle

a) The expectation value is

$$\langle E \rangle = \frac{\langle \psi(r) | \hat{H} | \psi(r) \rangle}{\langle \psi(r) | \psi(r) \rangle} \ge E_0 \tag{55}$$

which is the basis of the variational approach. We shall start by normalizing the wave function where the probability density plays a key role

$$\int |\psi(r)|^2 d^3 \mathbf{r} = \int_0^\infty A^2 e^{-2br^2} \cdot 4\pi r^2 dr \tag{56}$$

$$=4\pi A^2 \int_0^\infty r^2 e^{-2br^2} dr = 1.$$
 (57)

Note that we must use spherical coordinates now. The integral can be computed two ways by using the equations in the formula sheet. However, special care needs to be taken in terms of the integration limits $(r \ge 0)$. Let us use the equation

$$\int_{0}^{\infty} x^{2} e^{-ax^{2}} dx = \frac{\Gamma\left(\frac{3}{2}\right)}{2a^{3/2}}, \quad \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}.$$
(58)

This gives

$$\int_0^\infty r^2 e^{-2br^2} dr = \frac{\sqrt{\pi}}{4(2b)^{3/2}} \quad \to \quad A^2 = \left(\frac{2b}{\pi}\right)^{3/2},\tag{59}$$

and

$$\psi(r) = \left(\frac{2b}{\pi}\right)^{3/4} e^{-2br^2}.$$
(60)

b) The potential energy comes from the Coulomb potential and can be written as a

$$V(b) = -\frac{e^2}{4\pi\epsilon_0} \int |\psi(r)|^2 \frac{1}{r} d^3 \mathbf{r}$$
(61)

$$= -\frac{e^2}{4\pi\epsilon_0}A^2 \cdot 4\pi \int_0^\infty r e^{-2br^2} dr = -\frac{e^2}{\epsilon_0}A^2 \cdot \frac{1}{4b},$$
 (62)

where we have used a table integral in the formula sheet

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad \to \quad \int_0^\infty r e^{-2br^2} dr = \frac{1}{2(2b)}.$$
 (63)

Substituting A at this stage leads to the result

$$V(b) = -\frac{e^2}{\epsilon_0} \cdot \frac{\sqrt{2b}}{2\pi^{3/2}}.$$
 (64)

c) The kinetic energy involves the Laplacian

$$\nabla^2 \psi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r)}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \cdot \left(-2br^2 A e^{-br^2} \right) \right)$$
(65)

$$= -6br^2Ae^{-br^2} + 4br^4Ae^{-br^2}.$$
 (66)

Insert this to the integral for kinetic energy

$$T(b) = -\frac{\hbar^2}{2m} \int \psi(r) \nabla^2 \psi(r) d^3 \mathbf{r}$$
(67)

$$= \frac{\hbar^2}{2m} A^2 \cdot 4\pi \left[6b \int_0^\infty r^2 A e^{-2br^2} dr - 4b^2 \int_0^\infty r^4 A e^{-2br^2} dr \right].$$
(68)

Again, we are dealing with Gaussian integrals

$$\int_0^\infty r^2 e^{-2br^2} dr = \frac{\Gamma\left(\frac{3}{2}\right)}{2(2b)^{3/2}} = \frac{\frac{1}{2}\Gamma\left(\frac{1}{2}\right)}{2(2b)^{3/2}} = \frac{\sqrt{\pi}}{4(2b)^{3/2}},\tag{69}$$

$$\int_0^\infty r^4 e^{-2br^2} dr = \frac{\Gamma\left(\frac{5}{2}\right)}{2(2b)^{3/2}} = \frac{\frac{3}{2}\Gamma\left(\frac{3}{2}\right)}{2(2b)^{3/2}} = \frac{3\sqrt{\pi}}{8(2b)^{3/2}}.$$
(70)

Substitute these results and write out A^2

$$T(b) = \frac{\hbar^2}{2m} \cdot \left(\frac{2b}{\pi}\right)^{3/2} \cdot 4\pi \left[6b \cdot \frac{\sqrt{\pi}}{4(2b)^{3/2}} - 4b^2 \cdot \frac{3\sqrt{\pi}}{8(2b)^{3/2}}\right]$$
(71)

$$= \frac{\hbar^2}{2m} \cdot 4\left(\frac{6b}{4} - 4b^2 \cdot \frac{3}{16b}\right) = \frac{\hbar^2}{2m}(6b - 3b)$$
(72)

$$=\frac{3\hbar^2}{2m}b.$$
(73)

d) The total energy E(b) becomes

$$E(b) = T(b) + V(b) = \frac{3\hbar^2}{2m}b - \frac{e^2}{\epsilon_0} \cdot \frac{\sqrt{2b}}{2\pi^{3/2}}.$$
(74)

Take the derivative

$$\frac{dE(b)}{db} = \frac{3\hbar^2}{2m} - \frac{e^2}{2\epsilon_0} \cdot \frac{\sqrt{2}}{2\pi^{3/2}} \cdot b^{-1/2} = 0$$
(75)

and solve

$$b^{-1/2} = \frac{3\sqrt{2}\hbar^2 \pi^{3/2} \epsilon_0}{e^2 m} \quad \to \quad b = \frac{e^4 m^2}{18\hbar^4 \pi^3 \epsilon_0^2}.$$
 (76)

Substitute this to the expressions for kinetic and potential energy

$$T(b) = \frac{3\hbar^2}{2m} \cdot \frac{e^4 m^2}{18\hbar^4 \pi^3 \epsilon_0^2} = \frac{e^4 m}{12\hbar^2 \pi^3 \epsilon_0^2},\tag{77}$$

$$V(b) = -\frac{e^2}{\epsilon_0} \cdot \frac{\sqrt{2}}{2\pi^{3/2}} \cdot \sqrt{\frac{e^4 m^2}{18\hbar^4 \pi^3 \epsilon_0^2}} = -\frac{e^4 m}{6\hbar^2 \pi^3 \epsilon_0^2}.$$
 (78)

Hence, the optimized total energy becomes

$$E(b_{\min}) = -\frac{e^4 m}{12\hbar^2 \pi^3 \epsilon_0^2} \quad (\ge E_0).$$
⁽⁷⁹⁾

e) Let us calculate the numerical value for the optimized total energy by plugging in the physical constants. The unit conversions require some consideration. For example, the exponent of the numerator becomes less than -100 (if one uses the standard SI units) which cannot be handled by many (simple) calculators.

As expected, the numerical value $E_{\min} = -11.5$ eV is higher than the exact answer -13.6 eV. The overestimation is 15%, *i.e.* quite sizeable still. By comparing the trial function (Gaussian-type) with the exact solution of the ground state wave function of hydrogen atom $\psi(r) \sim e^{-r/a_0}$, one can conclude that despite the decaying profile there is considerable difference as $r \to 0$. The derivative of the exact solution (Slater-type function) does not go to zero but there is a "cusp" at r = 0. However, in practice, quantum chemists use trial wave functions that comprise linear combinations of (many) Gaussian functions because of their nice analytical properties while taking integrals (meaning that there is no need for numerical integration). We have just evidenced this in problems (a-c)!