Test Solutions - Not for distribution...

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1 Test A

1.

a) It is enough to show that the operators which make up the perturbation, $\hat{L}_z$ and $\hat{S}_z$, are commutative with the operators appearing in $\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{2\mu r^2}\hat{\mathbf{L}}^2 - \frac{Ze^2}{r}$. The simplest way to do this is to notice that the set of eigenfunctions of $\hat{H}_0$, $\psi_{n\ell m}\chi_{m_s}$, are also eigenfunctions of $\hat{L}_z$ and $\hat{S}_z$ having the eigenvalues $m\hbar$ and $m_s\hbar$ respectively. A slightly more complicated solution is to notice that $\hat{S}_z$ is defined within the spin subspace, unlike any operator within $\hat{H}_0$, and must therefore be commutative with it. Similarly, $\hat{L}_z$ works within the angular subspace and is therefore commutative with all radial terms; however, one must still show that $\left[\hat{L}_z, \hat{\mathbf{L}}^2\right] = 0$. This was shown in class.

b) In the basis of the $\psi_{n\ell m}\chi_{m_s}$, this is simply a matter of applying the operators:

$$\begin{aligned}\hat{H}\psi_{n\ell m}\chi_{m_s} &= \hat{H}_0\psi_{nlm}\chi_{m_s} - \frac{E_h}{2\hbar}B_a\left(\hat{L}_z + 2\hat{S}_z\right)\psi_{nlm}\chi_{m_s}\\ &= -\frac{E_h}{n^2}\psi_{nlm}\chi_{m_s} - \frac{E_h}{2\hbar}B_a\left(\hbar m + 2\hbar m_s\right)\psi_{nlm}\chi_{m_s}\\ &= \left[-\frac{E_h}{n^2} - \frac{E_h}{2\hbar}B_a\left(\hbar m + 2\hbar m_s\right)\right]\psi_{nlm}\chi_{m_s},\end{aligned}$$

or

$$\boxed{E_{n\ell m m_s} = -\frac{E_h}{n^2} - \frac{E_h}{2\hbar}B_a\left(\hbar m + 2\hbar m_s\right)}.$$

c) The possibilities which exist for $n = 1$ and $n = 2$ are as follows:

d) This Hamiltonian does not, in fact, have a ground state: we can take $n \to \infty$, $m \to \infty$ and obtain an infinite series of descending energies (the correct Hamiltonian has the additional a term $\sim \ell(\ell+1)$). If we treat the additional

n	ℓ	m	m_s	$E_{n\ell mm_s}$
1	0	0	$\pm\frac{1}{2}$	$E_{100\pm\frac{1}{2}} = E_h\left(-1 \mp \frac{7}{16}\right)$
2	0	0	$\pm\frac{1}{2}$	$E_{200\pm\frac{1}{2}} = E_h\left(-\frac{1}{4} \mp \frac{7}{16}\right)$
	1	0	$\pm\frac{1}{2}$	$E_{210\pm\frac{1}{2}} = E_h\left(-\frac{1}{4} \mp \frac{7}{16}\right)$
	1	1	$\pm\frac{1}{2}$	$E_{211\pm\frac{1}{2}} = E_h\left(-\frac{1}{2} - \frac{7}{16} \mp \frac{7}{16}\right)$
	1	-1	$\pm\frac{1}{2}$	$E_{21-1\pm\frac{1}{2}} = E_h\left(-\frac{1}{2} + \frac{7}{16} \mp \frac{7}{16}\right)$

potential as a perturbation and consider only its effect on the $n = 1$ and $n = 2$ levels as suggested by the question, the two lowest energies are given by

$$\boxed{E_{100\frac{1}{2}} = -\frac{23}{16}E_h,\ E_{211\frac{1}{2}} = -\frac{18}{16}E_h}.$$

2.

a) The Hamiltonian is separable, and (as in ex. 5, q. 5 for 2D)

$$E_{000} = \boxed{\frac{3}{2}\hbar\omega},$$

$$\psi_{000} = \psi_0(x)\,\psi_0(y)\,\psi_0(z) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\frac{\alpha x^2}{2} - \frac{\alpha y^2}{2} - \frac{\alpha z^2}{2}} = \boxed{\left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\frac{\alpha r^2}{2}}}.$$

Here, $\alpha \equiv \frac{m\omega}{\hbar}$.

b) We expand $V(r) = -De^{-\frac{r^2}{2\sigma^2}}$ in a second-order taylor series around $r = 0$. We will need:

$$\begin{aligned}
V(0) &= -D, \\
\frac{\partial V(0)}{\partial r} &= D\frac{r}{\sigma^2}e^{-\frac{r^2}{2\sigma^2}}\bigg|_{r=0} = 0, \\
\frac{\partial^2 V(0)}{\partial r^2} &= D\frac{1}{\sigma^2}e^{-\frac{r^2}{2\sigma^2}} - D\frac{r^2}{\sigma^4}e^{-\frac{r^2}{2\sigma^2}}\bigg|_{r=0} = \frac{D}{\sigma^2}.
\end{aligned}$$

With this,

$$V(r) \simeq V(0) + r\frac{\partial V(0)}{\partial r} + \frac{1}{2}r^2\frac{\partial^2 V(0)}{\partial r^2} = -D + \frac{1}{2}\frac{D}{\sigma^2}r^2.$$

Comparing with the expression for a harmonic oscillator, we find

$$\frac{1}{2}m\omega^2 r^2 = \frac{1}{2}\frac{D}{\sigma^2}r^2 \Rightarrow \boxed{\omega = \sqrt{\frac{D}{m\sigma^2}}}.$$

c) We compute the variational energy ε using the state from (a) and the frequency from (b):

$$\begin{aligned}\varepsilon &= \langle\psi|\,\hat{H}\,|\psi\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int \mathrm{d}^3r\, e^{-\frac{\alpha r^2}{2}}\left(-\frac{\hbar^2\nabla^2}{2m} - De^{-\frac{r^2}{2\sigma^2}}\right)e^{-\frac{\alpha r^2}{2}} \\ &= \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int \mathrm{d}^3r\, e^{-\frac{\alpha r^2}{2}}\left(-\frac{\hbar^2\nabla^2}{2m}\right)e^{-\frac{\alpha r^2}{2}} - \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int \mathrm{d}^3r\, e^{-\frac{\alpha r^2}{2}}De^{-\frac{r^2}{2\sigma^2}}e^{-\frac{\alpha r^2}{2}}.\end{aligned}$$

Now, both of these integrals are of the Gaussian form and can be computed exactly. However, it is not actually necessary to do the first one since it's exactly the kinetic energy of the ground state of a 3D oscillator, which we know to be half the total energy $\frac{3}{2}\hbar\omega$. Therefore, we are left only with the task of writing the second integral in terms of the given formula:

$$\begin{aligned}\varepsilon &= \frac{3}{4}\hbar\omega - \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int \mathrm{d}^3r\, e^{-\frac{\alpha r^2}{2}}De^{-\frac{r^2}{2\sigma^2}}e^{-\frac{\alpha r^2}{2}} \\ &= \frac{3}{4}\hbar\omega - \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}D\int \mathrm{d}^3r\, e^{-\left(\alpha+\frac{1}{2\sigma^2}\right)r^2} \\ &= \frac{3}{4}\hbar\omega - \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}D\frac{\pi^{\frac{3}{2}}}{\left(\alpha+\frac{1}{2\sigma^2}\right)^{\frac{3}{2}}} \\ &= \boxed{\frac{3}{4}\hbar\omega - D\sqrt{\frac{\alpha^3}{\left(\alpha+\frac{1}{2\sigma^2}\right)^3}}},\end{aligned}$$

where $\alpha = \frac{m\omega}{\hbar} = \sqrt{\frac{mD}{\hbar^2\sigma^2}}$.

2 Test B

1.

a) The ground state of the harmonic oscillator, as we have seen in class, is

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{\alpha x^2}{2}},$$

where $\alpha = \frac{m\omega}{\hbar}$. Here, with $\hat{V} = \frac{1}{2}\omega^2x^2$, we have taken $m = 1$. The 1^{st} order perturbation is the energy is therefore given by

$$\begin{aligned}\Delta E^{(1)} &= \left\langle\psi_0\right|\hat{W}\left|\psi_0\right\rangle = \left\langle\psi_0\left|W_0e^{-\frac{x^2}{2\sigma^2}}\right|\psi_0\right\rangle \\ &= \sqrt{\frac{\alpha}{\pi}}W_0\int \mathrm{d}x\, e^{-\frac{\alpha x^2}{2}}e^{-\frac{x^2}{2\sigma^2}}e^{-\frac{\alpha x^2}{2}} = \sqrt{\frac{\alpha}{\pi}}W_0\int \mathrm{d}x\, e^{-\left(\alpha+\frac{1}{2\sigma^2}\right)x^2} \\ &= W_0\sqrt{\frac{\alpha}{\pi}}\sqrt{\frac{\pi}{\alpha+\frac{1}{2\sigma^2}}} = \boxed{W_0\sqrt{\frac{\alpha}{\alpha+\frac{1}{2\sigma^2}}} = W_0\sqrt{\frac{\frac{\omega}{\hbar}}{\frac{\omega}{\hbar}+\frac{1}{2\sigma^2}}}}.\end{aligned}$$

To obtain the perturbed ground state energy, we need only add the zeroth-order term:

$$\begin{aligned} E^{(1)} &= E^{(0)} + \Delta E^{(1)} \\ &= \boxed{\frac{1}{2}\hbar\omega + W_0\sqrt{\frac{\frac{\omega}{\hbar}}{\frac{\omega}{\hbar}+\frac{1}{2\sigma^2}}}}. \end{aligned}$$

b) The variational energy ε is identical to the expression obtained in 1a:

$$\varepsilon = \left\langle \psi_0 \left| \hat{H} \right| \psi_0 \right\rangle \left\langle \psi_0 \left| \hat{H}_0 + \hat{W} \right| \psi_0 \right\rangle = \frac{1}{2}\hbar\omega + \sqrt{\frac{\alpha}{\alpha+\frac{1}{2\sigma^2}}} = \boxed{\frac{1}{2}\hbar\omega + W_0\sqrt{\frac{\frac{\omega}{\hbar}}{\frac{\omega}{\hbar}+\frac{1}{2\sigma^2}}}}.$$

c) Now, rather than immediately taking $\alpha = \frac{m\omega}{\hbar}$ as in the unperturbed system, we allow the value of α (not σ, which is a given constant!) to vary. As the hint points out, the term $\frac{1}{2}\hbar\omega$ in the variational energy also changes and must be recalculated:

$$\begin{aligned} \left\langle \psi_0^\omega \left| \hat{H}_0 \right| \psi_0^\omega \right\rangle &= \left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \left| -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \right| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \right\rangle \\ &= -\frac{\hbar^2}{2m}\left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \middle| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{\partial^2}{\partial x^2} e^{-\frac{\alpha x^2}{2}} \right\rangle \\ &\quad + \frac{1}{2}m\omega^2 \overbrace{\left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \left| x^2 \right| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \right\rangle}^{\equiv I(\alpha)} \\ &= -\frac{\hbar^2}{2m}\left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \middle| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{\partial}{\partial x}\left(-\alpha x e^{-\frac{\alpha x^2}{2}}\right) \right\rangle \\ &\quad + \frac{1}{2}m\omega^2 I(\alpha) \\ &= -\frac{\hbar^2}{2m}\left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \middle| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \left(-\alpha e^{-\frac{\alpha x^2}{2}} + \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}\right) \right\rangle \\ &\quad + \frac{1}{2}m\omega^2 I(\alpha) \\ &= \frac{\hbar^2}{2m}\alpha \overbrace{\left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \middle| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \right\rangle}^{=1} - \frac{\hbar^2\alpha^2}{2m} I(\alpha) \\ &\quad + \frac{1}{2}m\omega^2 I(\alpha). \end{aligned}$$

The remaining integral is

$$I(\alpha) = \left\langle \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \middle| x^2 \middle| \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \right\rangle = \sqrt{\frac{\alpha}{\pi}} \times \int \mathrm{d}x\, x^2 e^{-\alpha x^2}$$
$$= \sqrt{\frac{\alpha}{\pi}} \times \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}} = \frac{1}{2\alpha},$$

such that

$$\varepsilon(\alpha) = \frac{\hbar^2 \alpha}{4m} + \frac{m\omega^2}{4\alpha} + W_0\sqrt{\frac{\alpha}{\alpha + \frac{1}{2\sigma^2}}}.$$

The minimum is obtained when the derivative of ε with respect to α is zero, or

$$\frac{\partial \varepsilon(\alpha)}{\partial \alpha} = \frac{\hbar^2}{4m} - \frac{m\omega^2}{8\alpha^2} + \frac{\partial}{\partial \alpha}\sqrt{\frac{\alpha}{\alpha + \frac{1}{2\sigma^2}}} = \frac{\hbar^2}{4m} - \frac{m\omega^2}{8\alpha^2} + W_0 \frac{1}{2\sqrt{\frac{\alpha}{\alpha + \frac{1}{2\sigma^2}}}} \frac{\partial}{\partial \alpha} \frac{\alpha}{\alpha + \frac{1}{2\sigma^2}}$$
$$= \boxed{\frac{\hbar^2}{4m} - \frac{m\omega^2}{8\alpha^2} + \frac{W_0}{2\sqrt{\frac{\alpha}{\alpha + \frac{1}{2\sigma^2}}}} \left[\frac{1}{\alpha + \frac{1}{2\sigma^2}} - \frac{\alpha}{\left(\alpha + \frac{1}{2\sigma^2}\right)^2}\right] = 0}.$$

This is as far as one can take things during a test.

d) The energy of the first two cases is identical; the energy of 1c is either lower or equal to the first two, since the variational energy is bound from below by the ground state and is expected to come closer to it when an extra degree of freedom is added to it.

2.

a) We have obtained in class

$$\boxed{\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}},\ E_{100} = -\frac{Z^2 e^2}{2a_0}}.$$

b) We are simply being asked to subtract the energy above from the energy obtained by replacing the nuclear charge multiplicity Z by $Z+1$:

$$\Delta E_{\text{exact}} = -\frac{(Z+1)^2 e^2}{2a_0} - \left(-\frac{Z^2 e^2}{2a_0}\right) = \boxed{-\frac{(2Z+1)e^2}{2a_0} = -\frac{e^2 Z}{a_0} - \frac{e^2}{2a_0}}.$$

c) The perturbation $\hat{V}$ is the difference between the two Hamiltonians,

$$\hat{V} = \hat{H}_{Z+1} - \hat{H}_Z = -\frac{(Z+1)e^2}{r} - \left(-\frac{Ze^2}{r}\right) = -\frac{e^2}{r}.$$

The change in the ground state energy within 1st order perturbation theory is then given by the expectation value of $\hat{V}$ with respect to the unperturbed ground state:

$$\begin{aligned}
\Delta E^{(1)} &= \left\langle \psi_{100} \right| - \frac{e^2}{r} \left| \psi_{100} \right\rangle \\
&= -\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \int \mathrm{d}^3 r\, e^{-\frac{2Zr}{a_0}} \frac{e^2}{r} \\
&= -\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \overbrace{\int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \sin\vartheta \mathrm{d}\vartheta}^{=4\pi} \int_0^\infty r^2 \mathrm{d}r\, e^{-\frac{2Zr}{a_0}} \frac{e^2}{r} \\
&= -4e^2 \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r \mathrm{d}r\, e^{-\frac{2Zr}{a_0}}.
\end{aligned}$$

We have seen this type of integral in class; in order to solve it, we make the substitution $y = \frac{2Zr}{a_0} \Rightarrow r = \frac{a_0}{2Z} y \Rightarrow \mathrm{d}r = \frac{a_0}{2Z}\mathrm{d}y$, or

$$\Delta E^{(1)} = -4e^2 \left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^2 \overbrace{\int_0^\infty y \mathrm{d}y\, e^{-y}}^{=1!=1} = \boxed{-\frac{e^2 Z}{a_0}}.$$

d) The answer of (c) is an approximation, while the result of 2b is exact. The second term can be captured by going to higher order perturbation theory.