FALL 2021 EXAMINATION I
Duration: Take home (due Wednesday 13th October 5:30 pm)
There are 6 questions (total 30 marks). Answer all questions.
A permitted calculator may be used. Exams should be completed independently. Any copying will penalized with a 50% score reduction.

---

1. (6 marks) Using tables of the spherical harmonics ($Y_{l,m_l}(\theta, \phi)$) and radial solutions to the hydrogen atom ($R_{nl}(r)$), write down the form of the following hydrogen (Z=1) wavefunctions:

a) 3s (m_l=0)

b) 3d (m_l=0)

a) $\psi_{3,0,0}(r,\theta,\phi) = R_{3,0}(r)Y_{0,0}(\theta,\phi) = \left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(\frac{1}{243}\right)^{\frac{1}{2}}\left(6-6\left\{\frac{2r}{3a_0}\right\}+\left\{\frac{2r}{3a_0}\right\}^2\right)\exp\left\{-\frac{(2r/3a_0)}{2}\right\}\times\left(\frac{1}{2\pi^{1/2}}\right)$
$\psi_{3,0,0}(r,\theta,\phi) = \left(\frac{1}{972\pi a_0^3}\right)^{\frac{1}{2}}\left(6-\frac{4r}{a_0}+\frac{4r^2}{9a_0^2}\right)\exp\left\{-\frac{r}{3a_0}\right\})$

b) $\psi_{3,2,0}(r,\theta,\phi) = R_{3,2}(r)Y_{2,0}(\theta,\phi) = \left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(\frac{1}{2430}\right)^{\frac{1}{2}}\left(\frac{2r}{3a_0}\right)^2\exp\left\{-\frac{(2r/3a_0)}{2}\right\}\times\frac{1}{4}\left(\frac{5}{\pi}\right)^{\frac{1}{2}}(3\cos^2\theta-1)$
$\psi_{3,2,0}(r,\theta,\phi) = \left(\frac{1}{39366\pi a_0^7}\right)^{\frac{1}{2}}(3\cos^2\theta-1)r^2\exp\left\{-\frac{r}{3a_0}\right\})$

2. (6 marks) What is the wavelength of the photon emitted when a particle of mass 3.1 m_e in a box of length 2.2 a_0 decays from the first excited state to the ground state?

$E_n = 4\pi^2 n^2/8mL^2$
$E_2 - E_1 = (16\pi^2/8mL^2) - (4\pi^2/8mL^2) = 3\pi^2/2mL^2 = 0.987$ Hartree $= 4.303 \times 10^{-18}$ J
$\lambda = hc/E = 6.626 \times 10^{-34}$J s $\times 2.998 \times 10^8$m s^{-1}$/4.303 \times 10^{-18}$J $= 4.616 \times 10^{-8}$m $= 46$ nm

3. (6 marks) For the ground state of the particle in a harmonic oscillator, compute the expectation value for the position ($\langle x\rangle$), position squared ($\langle x^2\rangle$), and the uncertainty in the position ($\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$).

The ground state of the harmonic oscillator is:
$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$, where $\alpha = \left(\frac{km}{\hbar^2}\right)^{1/2}$
$\langle x\rangle = \int_{-\infty}^{+\infty} dx x|\psi_0(x)|^2 = \int_{-\infty}^{+\infty} dx x\left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2}$
$\langle x\rangle = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty} dx x e^{-\alpha x^2} = \left(\frac{\alpha}{\pi}\right)^{1/2}\left[-\frac{1}{2\alpha}e^{-\alpha x^2}\right]_{-\infty}^{+\infty} = 0$
$\langle x^2\rangle = \int_{-\infty}^{+\infty} dx x^2|\psi_0(x)|^2 = \int_{-\infty}^{+\infty} dx x^2\left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2} = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty} dx x^2 e^{-\alpha x^2}$
$\langle x^2\rangle = \left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}} = \frac{1}{2\alpha}$

$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \sqrt{\frac{1}{2\alpha} - 0} = \sqrt{\frac{\hbar}{2m^{1/2}k^{1/2}}}$

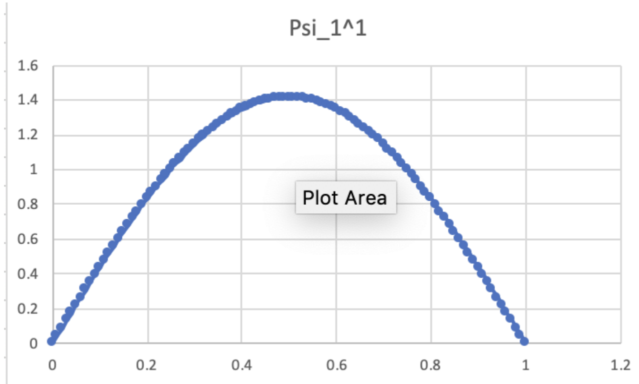
4. (12 marks) Using perturbation theory, calculate to first order the wavefunction of an arbitrary quantum state a of the particle in a box problem, modified by a constant potential in the region $0 \le x \le L$ of $y = Cx$, where C is a constant. Using an excel spreadsheet, plot the ground state wavefunction perturbed to first order by truncating the summation at $n = 10$. Draw the first-order perturbed wavefunction when $m = 1m_e$, $L = 1a_0$, in which a) $C = 0$, b) $C = 1$, c) $C = 100$. When the perturbation is small (i.e. $C = 1$) the first-order corrected wavefunction is a good approximation to the exact wavefunction. Explain the effect of the small perturbation on the wavefunction and why it makes sense in terms of the particle probability density.

The first-order perturbed wavefunction is:
$|\psi_a\rangle = |\psi_a^{(0)}\rangle + \sum_{b\neq a}\left\{\frac{\langle b|\hat{H}^{(1)}|a\rangle}{E_a^{(0)}-E_b^{(0)}}\right\}|\psi_b^{(0)}\rangle$
The denominator in the coefficients is:
$E_a^0 - E_b^0 = \frac{a^2h^2}{8mL^2} - \frac{b^2h^2}{8mL^2} = \frac{h^2}{8mL^2}(a^2-b^2) \Rightarrow \frac{\pi^2}{2mL^2}(a^2-b^2)$ Hartree
The numerator in the coefficients is:
$\langle a|Cx|b\rangle = \int_0^L dx\sqrt{\frac{2}{L}}\sin\left(\frac{a\pi}{L}x\right) \times Cx \times \sqrt{\frac{2}{L}}\sin\left(\frac{a\pi}{L}x\right) = \frac{2C}{L}\int_0^L dx x\sin\left(\frac{a\pi}{L}x\right)\sin\left(\frac{b\pi}{L}x\right)$
Use $\sin(ax)\sin(bx) = \frac{1}{2}\{\cos(ax-bx) - \cos(ax+bx)\}$
$\langle a|Cx|b\rangle = \frac{C}{L}\int_0^L dx x\cos\left((a-b)\frac{\pi}{L}x\right) - \frac{C}{L}\int_0^L dx x\cos\left((a-b)\frac{\pi}{L}x\right)$
Use integration by parts: $f = x$, $g' = \cos\left((a\pm b)\frac{\pi}{L}x\right)$, $f' = 1$, $g = \sin\left((a\pm b)\frac{\pi}{L}x\right) \times \frac{L}{(a\pm b)\pi}$
$\langle a|Cx|b\rangle = \frac{C}{L}\Big\{\left[\frac{xL}{(a-b)\pi}\sin\left((a-b)\frac{\pi}{L}x\right)\right]_0^L - \frac{L}{(a-b)\pi}\int_0^L dx\sin\left((a-b)\frac{\pi}{L}x\right) -$
. $\left[\frac{xL}{(a+b)\pi}\sin\left((a+b)\frac{\pi}{L}x\right)\right]_0^L + \frac{L}{(a+b)\pi}\int_0^L dx\sin\left((a+b)\frac{\pi}{L}x\right)\Big\}$
$\langle a|Cx|b\rangle = \frac{C}{L}\Big\{\frac{L^2}{(a-b)\pi}\xcancel{\sin((a-b)\pi)}^{0} - \frac{L}{(a-b)\pi}\left[\frac{-L}{(a-b)\pi}\cos\left((a-b)\frac{\pi}{L}x\right)\right]_0^L -$
. $\frac{L^2}{(a+b)\pi}\xcancel{\sin((a+b)\pi)}^{0} + \frac{L}{(a+b)\pi}\left[\frac{-L}{(a+b)\pi}\cos\left((a+b)\frac{\pi}{L}x\right)\right]_0^L\Big\}$
$\langle a|Cx|b\rangle = \frac{C}{L}\left\{\frac{L^2}{(a-b)^2\pi^2}(\cos((a-b)\pi)-1) - \frac{L^2}{(a+b)^2\pi^2}(\cos((a+b)\pi)-1)\right\}$
Use $\cos(2\theta) - 1 = -2\sin(\theta)$
$\langle a|Cx|b\rangle = \frac{CL}{\pi^2}\left\{\frac{1}{(a-b)^2}\Big(-2\sin\left((a-b)\frac{\pi}{2}\right) - \frac{1}{(a+b)^2}\Big(\sin\left((a+b)\frac{\pi}{2}\right)\right\}$
$\langle a|Cx|b\rangle = \frac{2CL}{\pi^2}\left\{\frac{1}{(a+b)^2}\Big(\sin\left((a+b)\frac{\pi}{2}\right) - \frac{1}{(a-b)^2}\Big(\sin\left((a-b)\frac{\pi}{2}\right)\right\}$
as from the particle in a box, a and b are integers:

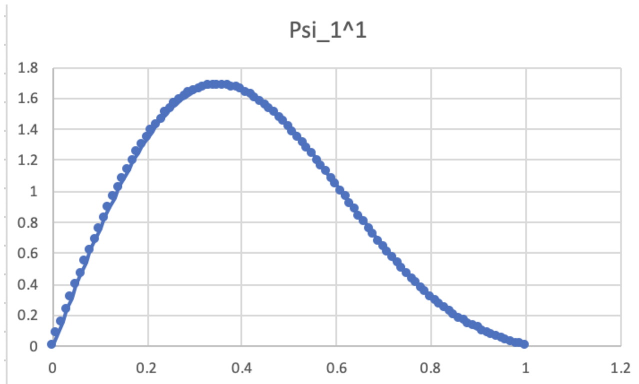
. if $(a+b)$ is even, then $(a-b)$ is even, and hence the argument to either sine function is an
. integer multiple of π, so that $\langle a|Cx|b\rangle = 0$
. if $(a+b)$ is odd, then $(a-b)$ is odd, and hence the argument to either sine function is a
. half-integer multiple of π, so that $\langle a|Cx|b\rangle = \frac{2CL}{\pi^2}\left\{\frac{1}{(a+b)^2} - \frac{1}{(a-b)^2}\right\}$

The first order perturbed wavefunction is therefore:

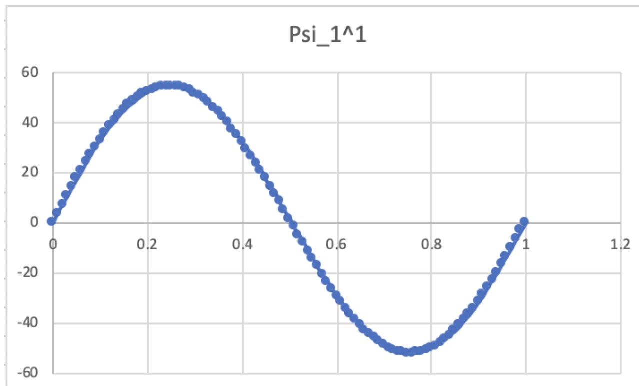
$$|\psi_a\rangle = |\psi_a^{(0)}\rangle + \sum_{b\forall a \bmod b=1}\frac{4mCL^3}{\pi^4(a^2-b^2)}\left\{\frac{1}{(a+b)^2} - \frac{1}{(a-b)^2}\right\}|\psi_b^{(0)}\rangle \quad (1)$$



First order perturbed wavefunction at $C = 0$.



First order perturbed wavefunction at $C = 1$.



First order perturbed wavefunction at $C = 100$.

The weak perturbation shifts the wavefunction, and hence the particle probability density to the left in the box. The change in wavefunction makes sense because the potential is higher on the right than the left.

END OF PAPER