HW3 = Solution Albers

and

$$\langle nljFm_F|\, \mathbf{s}_p\cdot\mathbf{s}_e\,|nljFm_F\rangle = \frac{1}{2j(j+1)}\left[j(j+1)-l(l+1)+\frac{3}{4}\right]\frac{1}{2}\left[F(F+1)-j(j+1)-\frac{3}{4}\right] \quad \text{(S7.141)}$$

Part f) Now add the two contributions for $l \neq 0$, separating out the terms with $\mathbf{s}_p\cdot\mathbf{s}_e$ from those with $\mathbf{s}_p\cdot\mathbf{L}$, and setting $g = 2$:

$$\langle nljFm_F|\, H'_{\text{dipole}} + H'_{\text{orbital}}\,|nljFm_F\rangle = \frac{g_p\alpha}{2Mm}\left\langle nl0\left|\frac{1}{r^3}\right|nl0\right\rangle [X_L + X_s] \quad \text{(S7.142)}$$

where

$$X_L = \left[1 - \frac{1}{(2l-1)(2l+3)}3\left(j(j+1)-l(l+1)-\frac{3}{4}\right)\right] \times \langle nljFm_F|\, \mathbf{s}_p\cdot\mathbf{L}\,|nljFm_F\rangle \quad \text{(S7.143)}$$

and

$$X_s = \frac{2l(l+1)}{(2l-1)(2l+3)}\langle nljFm_F|\, \mathbf{s}_p\cdot\mathbf{s}_e\,|nljFm_F\rangle \quad \text{(S7.144)}$$

Further simplify the expression by extracting the common factors is equations (S7.140) and (S7.141):

$$\langle nljFm_F|\, H'_{\text{dipole}} + H'_{\text{orbital}}\,|nljFm_F\rangle$$
$$= \frac{g_p\alpha}{2Mm}\left\langle nl0\left|\frac{1}{r^3}\right|nl0\right\rangle \frac{1}{2j(j+1)}\frac{1}{2}\left[F(F+1)-j(j+1)-\frac{3}{4}\right][Y_L+Y_s] \quad \text{(S7.145)}$$

where

$$Y_L = \left[1 - \frac{1}{(2l-1)(2l+3)}3\left(j(j+1)-l(l+1)-\frac{3}{4}\right)\right]\left[j(j+1)+l(l+1)-\frac{3}{4}\right] \quad \text{(S7.146)}$$

and

$$Y_s = \frac{2l(l+1)}{(2l-1)(2l+3)}\left[j(j+1)-l(l+1)-\frac{3}{4}\right] \quad \text{(S7.147)}$$

Setting $j = l+1/2$, after a little algebra the expression simplifies to $Y_L + Y_s = 2l(l+1)$. Setting $J = l - 1/2$, one gets $Y_L + Y_s = 2l(l+1)$ also! Therefore, when $l \neq 0$,

$$\langle nljFm_F|\, H'\,|nljFm_F\rangle = \frac{g_p\alpha}{4Mm}\left\langle nl0\left|\frac{1}{r^3}\right|nl0\right\rangle \frac{l(l+1)}{j(j+1)}\left[F(F+1)-j(j+1)-\frac{3}{4}\right] \quad \text{(S7.148)}$$

Finally (see Problem 3.21)

$$\left\langle nlm\left|\frac{1}{r^3}\right|nlm\right\rangle = \frac{\alpha^3m^3}{n^3l(l+\frac{1}{2})(l+1)} \quad \text{(S7.149)}$$

so the general formula is

$$\langle nljFm_F|\, H'\,|nljFm_F\rangle = \frac{g_p\alpha^4m}{2n^3}\left(\frac{m}{M}\right)\frac{1}{j(j+1)(2l+1)}\left[F(F+1)-j(j+1)-\frac{3}{4}\right] \quad \text{(S7.150)}$$

Part g) The $S$-state rule can be obtained from equation (S7.150) with $l = 0$ and $j = 1/2$. But the derivation was different.

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**Problem 7.13 Two Elementary Variational Method Problems**

Part a) The trial function is $\psi(x) = Ne^{-\beta|x|} = Ne^{-\beta x\Theta(x)}$. The normalization condition is

$$1 = N^2\int_{-\infty}^{\infty} e^{-2\beta|x|}\,dx = \frac{N^2}{\beta} \quad \text{(S7.151)}$$

whence $N^2 = \beta$. The derivatives are

$$\psi'(x) = -\beta N \left(e^{\beta x}\Theta(-x) + e^{-\beta x}\Theta(x)\right) \tag{S7.152}$$

and

$$\psi''(x) = \beta^2 N \left(e^{\beta x}\Theta(-x) + e^{-\beta x}\Theta(x)\right) - 2N\beta\delta\,(x) = \beta^2\psi(x) - 2N\beta\delta\,(x) \tag{S7.153}$$

The expectation value of the kinetic energy is

$$(\beta) = \left\langle \psi \middle| \frac{p^2}{2m} \middle| \psi \right\rangle = -\frac{1}{2m}\int_0^\infty \psi(x)\psi''(x)\,dx - \frac{\beta^2}{2m}\int_0^\infty |\psi(x)|^2\,dx + \frac{N}{m}\psi(0)^2 = \frac{\beta^2}{2m} \tag{S7.154}$$

The expectation value of the potential energy is

$$V(\beta) = N\int_0^\infty e^{-2\beta|x|}\frac{m\omega^2 x^2}{2}\,dx = \frac{N^2 m\omega^2}{(2\beta)^3}\int_0^\infty e^{-y}y^2\,dt = \frac{m\omega^2}{4\beta^2} \tag{S7.155}$$

so

$$E(\beta) = \frac{\beta^2}{2m} + \frac{m\omega^2}{4\beta^2} \tag{S7.156}$$

Since $E(\beta) \to \infty$ as $\beta \to 0$ and as $\beta \to \infty$, it has a minimum for some positive $\beta$. This occurs when $dE/d\beta = 0$, or

$$\beta^4 = \frac{1}{2}m^2\omega^2 \tag{S7.157}$$

For this value, $E(\beta) = \omega/\sqrt{2} = \sqrt{2}(\omega/2)$, greater than the correct energy by a factor $\sqrt{2}$.

Part b)

$$\psi(\mathbf{r}) = Ne^{-r^2/b^2} \tag{S7.158}$$

Compare this with the ground state wave function for the three-dimensional oscillator:

$$\psi(\mathbf{r}) = \left[\frac{m\omega}{\pi}\right]^{\frac{3}{4}} e^{-m\omega r^2/2} \tag{S7.159}$$

They are the same if we identify $m\omega = 2/b^2$, so

$$N = \left(\frac{2}{\pi b^2}\right)^{\frac{3}{4}} \tag{S7.160}$$

For a harmonic oscillator eigenstate, the expectation values of the kinetic and the potential energies are equal.[3] The kinetic energy is independent of the potential. So

$$\langle\psi|\,T\,|\psi\rangle = \frac{3}{4}\omega = \frac{3}{2mb^2} \tag{S7.161}$$

and

$$\langle\psi|\,V\,|\psi\rangle = -\int |\psi(\mathbf{r})|^2\frac{\alpha}{r}d^3r = -4\pi\alpha N^2\int_0^\infty e^{-2r^2/b^2}\frac{1}{2}d\left(r^2\right) = -\pi\alpha b^2\left(\frac{2}{\pi b^2}\right)^{\frac{3}{2}} = -\frac{\alpha}{b}\sqrt{\frac{8}{\pi}} \tag{S7.162}$$

Then with

$$E(b) = \langle\psi|\,T\,|\psi\rangle + \langle\psi|\,V\,|\psi\rangle \tag{S7.163}$$

the best value of $b$ is the solution to

$$0 = \frac{dE}{db} = -\frac{3}{mb^3} + \frac{\alpha}{b^2}\sqrt{\frac{8}{\pi}} \tag{S7.164}$$

At the value given by the solution,

$$E = -\frac{4\alpha^2 m}{3\pi} = -.4244131\ldots\alpha^2 m \tag{S7.165}$$

which, as expected, is slightly greater that the true value $-.5\alpha^2 m$.

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[3] This fact follows from the quantum virial theorem.

**Problem 7.14 Variational Estimate for a Quartic Potential**

Part a)

$$-\frac{1}{2m}\frac{d^2}{dx^2}\psi(x) + \lambda x^4\psi(x) = E\psi(x) \tag{S7.166}$$

Set $x = \beta t$:

$$-\frac{d^2}{dt^2}\psi(t) + \frac{2m\lambda\beta^6 t^4}{\hbar^2}\psi(t) = 2mE\beta^2\psi(t) \tag{S7.167}$$

Now choose $\beta^3 = 1/\sqrt{2m\lambda}$:

$$-\frac{d^2}{dt^2}\psi(t) + t^4\psi(t) = \frac{2mE}{\hbar^2}\left(\frac{1}{\sqrt{2m\lambda}}\right)^{\frac{2}{3}}\psi(t) = \bar{E}\psi(t) \tag{S7.168}$$

where

$$E_n = \bar{E}_n\left(\frac{\lambda}{4m^2}\right)^{\frac{1}{3}} \tag{S7.169}$$

Part b) The one-dimensional oscillator has ground state wave function

$$\psi(x) = \left[\frac{m\omega}{\pi}\right]^{\frac{1}{4}} e^{-m\omega x^2/2} \tag{S7.170}$$

So identify $m\omega = a^2$

$$N = \left(\frac{a^2}{\pi}\right)^{\frac{1}{4}} \tag{S7.171}$$

The functions $\psi(x)$ are eigenfunctions of a three-dimensional harmonic oscillator Hamiltonian with frequency $\omega$. For the oscillator, $\langle\psi|\, T\,|\psi\rangle = \langle\psi|\, V\,|\psi\rangle = E/2$ in any eigenstate. But the expectation vallue of $T$ does not know what the potential is, so here too the expectation value of the kinetic energy is

$$\langle\psi|\, T\,|\psi\rangle = \frac{\omega}{4} = \frac{a^2}{4m} \tag{S7.172}$$

Now set $2m = \lambda = 1$. Then [See equation (A.27)]

$$\langle\psi|\, V\,|\psi\rangle = N^2\int_{-\infty}^{\infty} x^4 e^{-a^2x^2}dx = \frac{a}{\sqrt{\pi}}\frac{1}{a^5}\int_{-\infty}^{\infty} y^4 e^{-y^2}dy = \frac{1}{a^4\sqrt{\pi}}\Gamma\left(\frac{5}{2}\right) = \frac{3}{4a^4} \tag{S7.173}$$

The scaled energy

$$\bar{E}(a) = \frac{a^2}{2} + \frac{3}{4a^4} \tag{S7.174}$$

is at a minimum when $a^6 = 3$. The best estimate of the energy is

$$\bar{E} = \frac{1}{4}3^{\frac{4}{3}} = 1.08169\ldots \tag{S7.175}$$

Then for any $\lambda$ and $m$,

$$\boxed{E(b) = 1.08169\ldots\left(\frac{\lambda\hbar^4}{4m^2}\right)^{\frac{1}{3}}} \tag{S7.176}$$

This energy is greater that the true ground state energy (as required) by about 2%.

Part c) The wave function for the first excited state of the one-dimensional oscillator is (see section 3.2.4)

$$\psi_1(x) = \sqrt{2m\omega}\left[\frac{m\omega}{\pi}\right]^{\frac{1}{4}} x e^{-m\omega x^2/2} \tag{S7.177}$$

**Problem 7.16 Variational Method for the Stark Effect on the Ground State of Atomic Hydroge**

Part a) The normalization is given by

$$\begin{aligned} 1 &= \int |\psi|^2 \, d^3r = N^2 \int e^{-2r/a} \left(1 + \frac{\beta}{a} r \cos\theta\right)^2 r^2 dr d\cos\theta \, d\phi \\ &= 2\pi N^2 \int e^{-2r/a} \left(1 + \frac{\beta^2}{a^2} r^2 \cos^2\theta\right) r^2 \, dr \, d\cos\theta \qquad \text{(S7.189} \\ &= 4\pi N^2 \left(\int_0^\infty e^{-2r/a} r^2 \, dr + \frac{\beta^2}{3a^2} \int_0^\infty e^{-2r/a} r^4 \, dr\right) = N^2 a^3 \pi \left(1 + \beta^2\right) \end{aligned}$$

so

$$N^2 = \frac{1}{a^3 \pi \left(1 + \beta^2\right)} \qquad \text{(S7.190}$$

Part b) The gradient of the wave function is

$$\nabla \psi(\mathbf{r}) = -\frac{1}{ar} N e^{-r/a} \left(1 + \frac{\beta}{a} z\right) \left[x \hat{n}_x + y \hat{n}_y + z \hat{n}_z\right] + N e^{-r/a} \frac{\beta}{a} \hat{n}_z \qquad \text{(S7.191}$$

so

$$\nabla \psi(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) = \frac{N^2}{a^2} e^{-2r/a} \left[\left(1 + \frac{\beta}{a} z\right)^2 \frac{x^2 + y^2 + z^2}{r^2} - \frac{2\beta z}{r} \left(1 + \frac{\beta z}{a}\right) + \beta^2\right] \qquad \text{(S7.192}$$

The expectation value of the kinetic energy is (terms linear in $z$ vanish upon integration)

$$\begin{aligned} T(\beta) &= -\frac{1}{2m} \int \psi(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) \, d^3r = \frac{1}{2m} \int \nabla \psi(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) \, d^3r \\ &= \frac{1}{2m} \frac{N^2}{a^2} \int e^{-2r/a} \left[1 + \beta^2 + \frac{\beta^2 z^2}{a} \left(\frac{1}{a} - \frac{2}{r}\right)\right] d^3r \\ &= \frac{1}{2m} \frac{N^2}{a^2} \int e^{-2r/a} \left[1 + \beta^2 + \frac{\beta^2 \cos^2\theta}{a} \left(\frac{r^2}{a} - 2r\right)\right] r^2 \, dr d\Omega \\ &= \frac{4\pi}{2m} \frac{N^2}{a^2} \int e^{-2r/a} \left[1 + \beta^2 + \frac{1}{3} \frac{\beta^2}{a} \left(\frac{r^2}{a} - 2r\right)\right] r^2 \, dr \qquad \text{(S7.193} \\ &= \frac{4\pi}{2m} \frac{N^2}{a^2} \left[\left(1 + \beta^2\right) \left(\frac{a}{2}\right)^3 \cdot 2 + \frac{1}{3} \frac{\beta^2}{a^2} \left(\frac{a}{2}\right)^5 \cdot 24 - \frac{2}{3} \frac{\beta^2}{a} \left(\frac{a}{2}\right)^4 \cdot 6\right] \\ &= \frac{2}{m} \frac{1}{a^2 \left(1 + \beta^2\right)} \left[\frac{1}{4}\left(1 + \beta^2\right) + \frac{1}{4}\beta^2 - \frac{1}{4}\beta^2\right] = \frac{1}{2ma^2} \end{aligned}$$

mysteriously independent of $\beta$. (There must be some way to understand this fact calculating.)

The expectation value of the Coulomb potential is

$$\begin{aligned} V_o(\beta) &= -\frac{1}{ma} \int |\psi(\mathbf{r})|^2 \frac{1}{r} d^3r = -N^2 \frac{1}{ma} \int e^{-2r/a} \left(1 + \frac{\beta z}{a}\right)^2 r \, dr d\Omega \\ &= -N^2 \frac{1}{ma} \int e^{-2r/a} \left(1 + \frac{\beta^2}{a^2} r^2 \cos^2\theta\right) r \, dr d\Omega = -4\pi N^2 \frac{1}{ma} \int e^{-2r/a} \left(1 + \frac{1}{3} \frac{\beta^2}{a^2} r^2\right) r \, dr \qquad \text{(S7.194} \\ &= -4\pi N^2 \frac{1}{ma} \left[\frac{a^2}{4} + \frac{1}{3} \frac{\beta^2}{a^2} \frac{a^4}{16} \cdot 6\right] = -\frac{\pi N^2 a}{m} \left(1 + \frac{\beta^2}{2}\right) = -\frac{1}{ma^2} \frac{1 + \frac{\beta^2}{2}}{1 + \beta^2} \end{aligned}$$

The expectation value of the electric field perturbation is

$$\begin{aligned}
H'(\beta) &= -eE\int |\psi(\mathbf{r})|^2\, r\cos\theta d^3r \\
&= N^2 eE\int e^{-2r/a}\left(1+\frac{\beta z}{a}\right)^2 r^3\cos\theta\, dr d\Omega = N^2 eE\frac{2\beta}{a}\int e^{-2r/a} r^4\cos^2\theta\, dr\, d\Omega \\
&= \frac{8\pi N^2\beta eE}{3a}\left(\frac{a}{2}\right)^5\cdot 24 = 2\pi N^2 eE\beta a^4 = 2eE\beta a\frac{1}{1+\beta^2}
\end{aligned} \tag{S7.195}$$

Part c) Thus the expectation value of the energy is

$$\begin{aligned}
E(\beta) &= \frac{1}{2ma^2} - \frac{1}{ma^2}\frac{1+\frac{\beta^2}{2}}{1+\beta^2} + 2eE\beta a\frac{1}{1+\beta^2} \\
&= \frac{1}{2ma^2} + \frac{1}{a^2}\frac{1}{1+\beta^2}\left(2eE\beta a^3 - \frac{1}{m}\left(1+\frac{\beta^2}{2}\right)\right) \\
&= \frac{1}{a^2}\frac{1}{1+\beta^2}\left(\frac{1+\beta^2}{2m} + 2eE\beta a^3 - \frac{1}{m}\left(1+\frac{\beta^2}{2}\right)\right) = \frac{1}{1+\beta^2}\left(2eE\beta a - \frac{1}{2ma^2}\right)
\end{aligned} \tag{S7.196}$$

Part d) There is a minimum when

$$\begin{aligned}
0 &= \frac{d}{d\beta}a^2 E(\beta) = -\frac{2\beta}{(1+\beta^2)^2}\left(2eE\beta a^3 - \frac{1}{2m}\right) + \frac{1}{1+\beta^2}2eEa \\
&= \frac{1}{(1+\beta^2)^2}\left[2eEa^3(1+\beta^2) - 2\beta\left(2eE\beta a^3 - \frac{1}{2m}\right)\right]
\end{aligned} \tag{S7.197}$$

or

$$0 = \beta^2 - \frac{\beta}{2eEa^3m} - 1 \tag{S7.198}$$

The solution is

$$\beta = \frac{1}{2}\left[\frac{1}{2eEa^3m} \pm \sqrt{\frac{1}{4e^2E^2a^6m^2} + 4}\right] = \frac{1}{4eEa^3m}\left[1 \pm \sqrt{1+16e^2E^2m^2a^6}\right] \tag{S7.199}$$

The negative sign yields the lower value if $eE$ is positive. At this value,

$$2eE\beta a = \frac{1}{2ma^2}\left[1 - \sqrt{1+16e^2E^2m^2a^6}\right] = -4e^2E^2ma^4 + \cdots \tag{S7.200}$$

and

$$\beta^2 = \frac{1}{8e^2E^2m^2a^6}\left[1 + 8e^2E^2m^2a^6 - \sqrt{1+16e^2E^2m^2a^6}\right] = 4e^2E^2m^2a^6 + \cdots \tag{S7.201}$$

The energy, to order $E^2$, is

$$\begin{aligned}
E &= \frac{1}{1+4e^2E^2m^2a^6}\left(-4e^2E^2ma^4 - \frac{1}{2ma^2}\right) + \cdots \\
&= -\left(1 - 4e^2E^2m^2a^6\right)\left(4e^2E^2ma^4 + \frac{1}{2ma^2}\right) + \cdots \\
&= -\frac{1}{2ma^2} - 4e^2E^2ma^4 + 2e^2E^2ma^4 + \cdots = -\frac{1}{2ma^2} - 2e^2E^2ma^4 + \cdots \\
&= \boxed{-\frac{1}{2ma^2} - 2E^2a^3 + \cdots}
\end{aligned} \tag{S7.202}$$