PSET 1

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1 Quantum Mechanics of a Particle in the Earth's Gravitational Field

We consider the quantum mechanics of a particle in the earth's gravitational field:

$$\begin{aligned} V(r) &= -\frac{GMm}{r} \\ &= -\frac{GMm}{R+z} \\ &\approx -\frac{GMm}{R} + mgz \end{aligned}$$

where

- M = mass of earth
- r = distance from center of earth
- G = Newton's gravitational constant
- R = radius of earth
- z = height of particle above surface of earth
- $g = \frac{GM}{R^2}$

We may drop the constant term in our discussion, and consider only the mgz piece, with $z \ll R$. We further assume that no angular momentum is involved, and treat as a one-dimensional problem. Finally, assume that the particle is unable to penetrate the earth's surface.

1.0.1 Question

Make a WKB calculation for the energy spectrum of the particle.

1.0.2 Answer

First, we want to figure out our classical turning points. Since the particle can't penetrate the earth's surface, we have:

$$V(z) = \begin{cases} mgz, & z \geq 0 \\ \infty, & z < 0 \end{cases} \tag{1}$$

So, we have that the classical turning points are $z_1 = 0$ and and where the potential becomes larger than the kinetic energy of the particle, which occurs at $z_2 = \frac{E}{mg}$. Also, we must note that $mgz \ll z$, so the approximation that our potential is slowly varying with the position is accurate, and thus it makes sense to apply the WKB approximation. Then, we can define the momentum as:

$$p = \sqrt{2m(E - mgz)} \tag{2}$$

So, the $f(E)$ is given by:

$$f(E) = \int_0^{\frac{E}{mg}} \sqrt{2m(E - mgz)}dz \tag{3}$$

Now, we make the substitution $u = E - mgz$, so $du = -mgdz$, and $dz = -\frac{du}{mg}$, and we get:

$$f(E) = -\frac{1}{mg}\int_E^0 \sqrt{2mu}du = \frac{1}{mg}\int_0^E \sqrt{2mu}du = \frac{2\sqrt{2}}{3g\sqrt{m}}(u^{\frac{3}{2}})_0^E = \frac{2\sqrt{2}}{3g\sqrt{m}}E^{\frac{3}{2}} \tag{4}$$

Now, we can use the WKB approximation to find the energy levels. As explained in office ours, for the infinite spare will, we derived in lecture that this would be a factor of $(n+1)\pi$, since both of the classical turning points are also the boundary conditions. In the lecture, we also did a case where the both classical turning points were not the boundary conditions, and then the factor was of $(n + \frac{1}{2})\pi$. In this case, we have one classical turning point as a boundary condition, and the other classical turning point as a classical turning point, so we expect the factor to be of $(n + \frac{3}{4})\pi$. So, we can write:

$$\frac{2\sqrt{2}}{3g\sqrt{m}}E^{\frac{3}{2}} = (n + \frac{3}{4})\pi\hbar \tag{5}$$

Solving for E_n, we get:

$$E_n = \sqrt[3]{\frac{9g^2\pi^2\hbar^2 m}{8}(n + \frac{3}{4})^2} \tag{6}$$

1.1 Estimation of the Particle's Ground State Energy

1.1.1 Question

If the particle is an atom of atomic weight $A \sim 100$, use the result of the WKB calculation to estimate the particle's ground state energy (in eV). Is sunlight likely to move the particle into excited states?

1.1.2 Answer

We know that one atomic weight is equal to 1.66×10^{-27} kg, so we can estimate the mass of the particle as 1.66×10^{-25} kg. Also, we know that $g = \frac{GM}{R^2}$, and we can look up the values of G, M, and R to get $g = 9.8$ m/s^2. So, we can plug these values into our equation for the ground state energy to with $n = 0$ to get:

$$
\begin{aligned}
E_0 &= \sqrt[3]{\frac{9g^2\pi^2\hbar^2 m}{8}(\frac{3}{4})^2} \\
&= \sqrt[3]{\frac{9(9.8)^2\pi^2(1.05 \times 10^{-34})^2(1.66 \times 10^{-25})}{8}(\frac{3}{4})^2} \\
&\approx 6.44 \times 10^{-12} \text{ eV}
\end{aligned}
$$

Sunlight is on the order of 10^0 eV, so it is unlikely to move the particle into excited states i.e. sunlight photons' energies are too large.

2 Variational Calculation for the Ground State Energy

2.0.1 Question

Continuing with the gravitational problem in problem 1, now make a variational calculation for the ground state energy (i.e., an upper bound thereon). Pick a "sensible" trial wave function, at least in the sense that it satisfies the right boundary conditions. Compare your result with the ground state level from the WKB approximation.

2.0.2 Answer

We will choose the trial wave function:

$$\psi(z) = Aze^{-\gamma z} \tag{7}$$

We note that in the limits as $z \to 0$ and $z \to \infty$, this wave function goes to zero, so it satisfies the right boundary conditions. Now, we normalize the wave function to find A:

$$
\begin{aligned}
1 &= \int_0^\infty |\psi(z)|^2 dz \\
&= \int_0^\infty A^2 z^2 e^{-2\gamma z} dz \\
&= A^2 \int_0^\infty z^2 e^{-2\gamma z} dz
\end{aligned}
$$

Now, we make the substitution $u = 2\gamma z$, so $z = \frac{u}{2\gamma}$, and $dz = \frac{du}{2\gamma}$, and we get:

$$\begin{aligned}
1 &= A^2 \int_0^\infty \left(\frac{u}{2\gamma}\right)^2 e^{-u} \frac{du}{2\gamma} \\
&= \frac{A^2}{8\gamma^3} \int_0^\infty u^2 e^{-u} du \\
&= \frac{A^2}{8\gamma^3} \Gamma(3) \\
&= \frac{A^2}{8\gamma^3} 2! \\
&= \frac{A^2}{4\gamma^3} \\
\implies A &= \boxed{2\gamma^{\frac{3}{2}}}
\end{aligned}$$

Now, we can calculate the expectation value of the energy:

$$\langle\psi|H|\psi\rangle = \int_0^\infty \psi^*(z) \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}z^2} + mgz\right) \psi(z) dz \tag{8}$$

First, we will work on the kinetic energy term:

$$KE = -\frac{A^2\hbar^2}{2m} \int_0^\infty ze^{-\gamma z} \frac{\mathrm{d}^2}{\mathrm{d}z^2} \left(ze^{-\gamma z}\right) dz$$

So, we know that:

$$\frac{d^2}{dz^2}\left(ze^{-\gamma z}\right) = \frac{d}{dz}\left(e^{-\gamma z} - \gamma z e^{-\gamma z}\right) = -2\gamma e^{-\gamma z} + \gamma^2 z e^{-\gamma z} \tag{9}$$

and then:

$$ze^{-\gamma z}\left(-2\gamma e^{-\gamma z} + \gamma^2 z e^{-\gamma z}\right) = -2\gamma z e^{-2\gamma z} + \gamma^2 z^2 e^{-2\gamma z} \tag{10}$$

Plugging this result in:

$$KE = -\frac{A^2\hbar^2}{2m} \int_0^\infty \left(-2\gamma z e^{-2\gamma z} + \gamma^2 z^2 e^{-2\gamma z}\right) dz$$

We wish to solve the integral and we can split it two pieces:

$$I_{11} = \int_0^\infty -2\gamma z e^{-2\gamma z} dz \tag{11}$$

Making the substitutions $u = 2\gamma z$, so $z = \frac{u}{2\gamma}$, and $dz = \frac{du}{2\gamma}$, we get:

$$\begin{aligned}
I_{11} &= \int_0^\infty -2\gamma \frac{u}{2\gamma} e^{-u} \frac{du}{2\gamma} \\
&= -\frac{1}{2\gamma} \int_0^\infty u e^{-u} du \\
&= -\frac{1}{2\gamma} \Gamma(2) \\
&= -\frac{1}{2\gamma} 1! \\
&= -\frac{1}{2\gamma}
\end{aligned}$$

Next, we have:

$$I_{12} = \int_0^\infty \gamma^2 z^2 e^{-2\gamma z} dz \tag{12}$$

Making the substitutions $u = 2\gamma z$, so $z = \frac{u}{2\gamma}$, and $dz = \frac{du}{2\gamma}$, we get:

$$\begin{aligned}
I_{12} &= \int_0^\infty \gamma^2 \left(\frac{u}{2\gamma}\right)^2 e^{-u} \frac{du}{2\gamma} \\
&= \frac{1}{8\gamma} \int_0^\infty u^2 e^{-u} du \\
&= \frac{1}{8\gamma} \Gamma(3) \\
&= \frac{1}{8\gamma} 2! \\
&= \frac{1}{4\gamma}
\end{aligned}$$

So:

$$KE = -\frac{A^2 \hbar^2}{2m} \left(-\frac{1}{2\gamma} + \frac{1}{4\gamma}\right) = \boxed{\frac{3A^2\hbar^2}{8m\gamma}} \tag{13}$$

Now, we can work on the potential energy term:

$$PE = A^2 mg \int_0^\infty z^3 e^{-2\gamma z} dz$$

Substituting $u = 2\gamma z$, so $z = \frac{u}{2\gamma}$, and $dz = \frac{du}{2\gamma}$, we get:

$$
\begin{aligned}
PE &= A^2 mg \int_0^\infty \left(\frac{u}{2\gamma}\right)^3 e^{-u} \frac{du}{2\gamma} \\
&= \frac{A^2 mg}{16\gamma^4} \int_0^\infty u^3 e^{-u} du \\
&= \frac{A^2 mg}{16\gamma^4} \Gamma(4) \\
&= \frac{A^2 mg}{16\gamma^4} 3! \\
&= \boxed{\frac{3A^2 mg}{8\gamma^4}}
\end{aligned}
$$

Now, we can calculate the expectation value of the energy:

$$
\begin{aligned}
\langle \psi | H | \psi \rangle &= KE + PE \\
&= \frac{3A^2\hbar^2}{8m\gamma} + \frac{3A^2 mg}{8\gamma^4}
\end{aligned}
$$

Substituting in For A:

$$
\begin{aligned}
\langle \psi | H | \psi \rangle &= \frac{3(2\gamma^{\frac{3}{2}})^2\hbar^2}{8m\gamma} + \frac{3(2\gamma^{\frac{3}{2}})^2 mg}{8\gamma^4} \\
&= \frac{12\gamma^3\hbar^2}{8m\gamma} + \frac{12\gamma^3 mg}{8\gamma^4} \\
&= \frac{3\gamma^2\hbar^2}{2m} + \frac{3mg}{2\gamma}
\end{aligned}
$$

Now, we can minimize this expression with respect to γ:

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}\gamma}\left(\frac{3\gamma^2\hbar^2}{2m} + \frac{3mg}{2\gamma}\right) &= 0 \\
\frac{6\gamma\hbar^2}{2m} - \frac{3mg}{2\gamma^2} &= 0
\end{aligned}
$$

Multiplying everything by γ^2 and $2m$:

$$\begin{aligned}6\gamma^3\hbar^2 - 3m^2 g = 0\\ \gamma^3 &= \frac{m^2 g}{2\hbar^2}\\ \gamma &= \left(\frac{m^2 g}{2\hbar^2}\right)^{\frac{1}{3}}\end{aligned}$$

Substituting in to find the minimum energy:

$$\begin{aligned}\langle\psi|H|\psi\rangle &= \frac{3\left(\frac{m^2 g}{2\hbar^2}\right)^{\frac{2}{3}}\hbar^2}{2m} + \frac{3mg}{2\left(\frac{m^2 g}{2\hbar^2}\right)^{\frac{1}{3}}}\\ &= \frac{3m^{\frac{1}{3}}g^{\frac{2}{3}}\hbar^{\frac{2}{3}}}{2^{\frac{8}{3}}} + \frac{3\hbar^{\frac{2}{3}}m^{\frac{1}{3}}g^{\frac{2}{3}}}{2^{\frac{2}{3}}}\end{aligned}$$

By plugging in the same valgus for g and m as we did in the WKB approximation, we get:

$$\begin{aligned}\langle\psi|H|\psi\rangle &= \frac{3(1.66\times10^{-25})^{\frac{1}{3}}(9.8)^{\frac{2}{3}}(1.05\times10^{-34})^{\frac{2}{3}}}{2^{\frac{8}{3}}} + \frac{3(1.05\times10^{-34})^{\frac{2}{3}}(1.66\times10^{-25})^{\frac{1}{3}}(9.8)^{\frac{2}{3}}}{2^{\frac{2}{3}}}\\ &\approx 8.26\times10^{-12}\ \text{eV}\end{aligned}$$

This is a bit higher than the WKB approximation, but it is still on the same order of magnitude.

3 Inequality on the Ground State Energy

3.0.1 Question

We can find other inequalities in the same spirit as our inequality on the ground state energy. For example, if we can find a lower bound on $E_1 - \langle\psi|H|\psi\rangle$, where E_1 is the first excited energy, and ψ is a trial wave function, the theorem below might be used to obtain a lower bound on E_0. Prove the theorem:

> Theorem: If we have a normalized function $|\psi\rangle$ such that
>
> $$E_0 \le \langle\psi|H|\psi\rangle \le E_1,$$
>
> then
>
> $$E_0 \ge \langle\psi|H|\psi\rangle - \frac{\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2}{E_1 - \langle\psi|H|\psi\rangle}.$$

3.0.2 Answer

We started by wringing some terms in the second equation:

$$\frac{\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2}{E_1 - \langle\psi|H|\psi\rangle} \geq \langle\psi|H|\psi\rangle - E_0 \tag{14}$$

Then, we multiplied both sides by $E_1 - \langle\psi|H|\psi\rangle$:

$$\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2 \geq (E_1 - \langle\psi|H|\psi\rangle)(\langle\psi|H|\psi\rangle - E_0) \tag{15}$$

Now we can shift by a constant, so that $E_0 = 0$:

$$\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2 \geq (E_1 - \langle\psi|H|\psi\rangle)\langle\psi|H|\psi\rangle \tag{16}$$

Now, we can expand the right hand side:

$$\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2 \geq E_1\langle\psi|H|\psi\rangle - \langle\psi|H|\psi\rangle^2$$

Now, we can add $\langle\psi|H|\psi\rangle^2$ from both sides:

$$\langle H\psi|H\psi\rangle \geq E_1\langle\psi|H|\psi\rangle$$

We want to prove that:

$$\langle H\psi|H\psi\rangle - E_1\langle\psi|H|\psi\rangle \geq 0 \tag{17}$$

At this point, we can expand in terms of the eigenstates of H:

$$\psi = \sum_n c_n |n\rangle \tag{18}$$

and

$$H|n\rangle = E_n|n\rangle \tag{19}$$

So, we can write:

$$E_1\langle\psi|H|\psi\rangle = E_1\sum_n c_n\langle\psi|H|n\rangle = E_1\sum_n c_n E_n\langle\psi|n\rangle = E_1\sum_m\sum_n c_m^* c_n E_n\delta_{mn} = E_1\sum_n |c_n|^2 E_n \tag{20}$$

On the other term, we have:

$$\langle H\psi|H\psi\rangle = \sum_m\sum_n c_m^* c_n\langle m|H^\dagger H|n\rangle = \sum_m\sum_n c_m^* c_n E_m E_n\delta_{mn} = \sum_n |c_n|^2 E_n^2 \tag{21}$$

We already made the shift, so that $E_0 = 0$, so we can write that $\forall n$:

$$\sum_n |c_n|^2 E_n^2 \geq E_1\sum_n |c_n|^2 E_n \tag{22}$$

Therefore we have that in equality in equation 17 is true, so we have proven the theorem.

4 Variational Approach to Ground State Energy Levels of Atoms

4.0.1 Question

Let us pursue our variational approach to the estimation of ground state energy levels of atoms for the "general" case. We consider an atom with nuclear charge Z, and N electrons. The Hamiltonian of interest is:

$$\begin{aligned} H(Z,N) &= H_{\text{kin}} - ZV_c + V_e \\ H_{\text{kin}} &= \sum_{n=1}^{N} \frac{p_n^2}{2m} \\ V_c &= \alpha \sum_{n=1}^{N} \frac{1}{|x_n|} \\ V_e &= \alpha \sum_{N \geq j > k \geq 1} \frac{1}{|x_k - x_j|} \end{aligned}$$

where

- m = electron mass
- α = fine structure constant.

Denote the ground state energy of $H(Z,N)$ by $-B(Z,N)$, with $B(Z,0) = 0$. Generalize the variational calculation we performed for the ground state of helium to the general Hamiltonian $H(Z,N)$. Thus, select your "trial function" to be a product of N identical "hydrogen atom ground state" functions. Determine the resulting lower bound $\hat{B}(Z,N)$ on $B(Z,N)$ (i.e., an upper limit on the ground state energies).

4.0.2 Answer

The hydration ground state wave function is given by:

$$\psi_{\text{hydrogen}} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{r}{a_0}} \tag{23}$$

The trial wave function will be a product of these:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \prod_{n=1}^{N} \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Z r_n}{a_0}} \tag{24}$$

First we want to compute the kinetic energy for this system:

$$\langle \Psi | \sum_{n=1}^{N} \frac{p_n^2}{2m} | \Psi \rangle = \sum_{n=1}^{N} \langle \Psi | \frac{p_n^2}{2m} | \Psi \rangle$$

We can, therefore, just consider one of these terms:

$$\langle\Psi|\, \frac{p_N^2}{2m}\, |\Psi\rangle = \int_{(\infty)} d^3\mathbf{x}_1 \int_{(\infty)} d^3\mathbf{x}_2 \cdots \int_{(\infty)} d^3\mathbf{x}_N\, \Psi^* \frac{p_N^2}{2m} \Psi \tag{25}$$

Inserting our expression for Ψ:

$$\begin{aligned}\langle\Psi|\, \frac{p_N^2}{2m}\, |\Psi\rangle &= \int_{(\infty)} d^3\mathbf{x}_1 \int_{(\infty)} d^3\mathbf{x}_2 \cdots \int_{(\infty)} d^3\mathbf{x}_N \prod_{n=1}^{N} \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr_n}{a_0}} \frac{p_N^2}{2m} \prod_{n=1}^{N} \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr_n}{a_0}} \\ &= \int_{(\infty)} d^3\mathbf{x}_1 \int_{(\infty)} d^3\mathbf{x}_2 \cdots \prod_{n=1}^{N-1} \frac{Z^3}{\pi a_0^3} e^{-\frac{2Zr_n}{a_0}} \int_{(\infty)} d^3\mathbf{x}_N \frac{Z^3}{\pi a_0^3} e^{-\frac{Zr_n}{a_0}} \frac{p_N^2}{2m} e^{-\frac{Zr_n}{a_0}}\end{aligned}$$

This is equal to:

$$\langle\Psi|\, \frac{p_N^2}{2m}\, |\Psi\rangle = Z^2 \times \text{kinetic energy of hydrogen atom crowned state} = Z^2 \times \frac{1}{2} m\alpha^2 \tag{26}$$

So,N of these terms gives us:

$$\langle\Psi|H_{\text{kin}}|\Psi\rangle = \frac{N}{2} m\alpha^2 Z^2 \tag{27}$$

Next, we consider the nuclear potential defined by V_c. As we showed in the lecture for the hydration crowned state function:

$$\langle\Psi|\frac{\alpha}{|\mathbf{x}_1|}|\Psi\rangle = Zm\alpha^2 \tag{28}$$

The Z here is a parameter that we want to vary, different from the Z in our Hamiltonian, so we will call the latter Z'. So, we have:

$$-Z'\, \langle\Psi|\frac{\alpha}{|\mathbf{x}_1|}|\Psi\rangle = -Z' Z m\alpha^2 \tag{29}$$

and N of these terms gives us:

$$\langle\Psi|-Z'V_c|\Psi\rangle = -Z' Z m\alpha^2 N \tag{30}$$

So, we currently have:

$$\langle\Psi|H_{\text{kin}} - Z'V_c|\Psi\rangle = \frac{1}{2} m\alpha 2 \left(NZ^2 - 2Z'ZN\right) \tag{31}$$

Now, we consider the electron-electron repulsion term for the case of the hilum atom where there was only two electrons. We can write this as:

$$\langle\Psi|\, \frac{\alpha}{r_{12}}\, |\Psi\rangle = \alpha \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_{(\infty)} d^3\mathbf{x}_1 \int_{(\infty)} d^3\mathbf{x}_2 e^{-\frac{2Zr_1}{a_0}} e^{-\frac{2Zr_2}{a_0}} \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \tag{32}$$

As shown in the lecture, this can be evaluated to:

$$\langle\Psi|\frac{\alpha}{r_{12}}|\Psi\rangle = \frac{1}{2}m\alpha^2\frac{5}{4}Z \tag{33}$$

This is only for one of the terms, and our summation is:

$$\sum_{N\geq j\geq k\geq 1} 1 = \sum_{j=1}^{N}\sum_{k=1}^{j-1} 1 = \sum_{j=1}^{N}(j-1) = \left(\sum_{j=1}^{N}\right) - N = \frac{N(N+1)}{2} - N = \frac{N(N-1)}{2} \tag{34}$$

So, we get:

$$\langle\Psi|V_e|\Psi\rangle = \frac{1}{2}m\alpha^2\frac{5}{4}Z\frac{N(N-1)}{2} \tag{35}$$

So, we have:

$$\begin{aligned}
&\langle\Psi|H_{\text{kin}} - Z'V_c + V_e|\Psi\rangle && (36)\\
&= \frac{1}{2}m\alpha 2\left(NZ^2 - 2Z'ZN + \frac{5}{8}ZN(N-1)\right) && (37)\\
&= \frac{N}{2}m\alpha 2\left(Z^2 - 2Z'Z + \frac{5(N-1)}{8}\right) && (38)
\end{aligned}$$

We now minimize with respect to the variational parameter Z:

$$0 = \frac{d\langle H\rangle}{dZ} \to 2Z - 2Z' + \frac{5(N-1)}{8} = 0 \implies Z = Z' - \frac{5(N-1)}{16} \tag{39}$$

So for the $B(Z,N)$ since it is defined as $-H(Z,N)$, we have:

$$\hat{B}(Z,N) = -\frac{N}{2}m\alpha 2\left(\left(Z' - \frac{5(N-1)}{16}\right)^2 + \left(Z' - \frac{5(N-1)}{16}\right)\left(\frac{5(N-1)}{8} - 2Z'\right)\right) \tag{40}$$

We can simplify this to:

$$= \boxed{+\frac{N}{2}m\alpha^2\left(Z' - \frac{5(N-1)}{16}\right)^2} \tag{41}$$