DEGENERATE PERTURBATION THEORY. In this problem, we are already given the wavefunctions of a particle confined in a ring. We then place a small Gaussian barrier $H' = V_0 \exp\left(-\dfrac{x^2}{a^2}\right)$. To solve for the corrections to the energy eigenvalues, we use degenerate perturbation theory, as the wavefunctions are doubly degenerate (same energy for two different wavefunctions n and $-n$ for $n \neq 0$).

The first-order correction can be found by solving the eigenvalues of the matrix with elements $\langle n\alpha|H'|n\beta\rangle$ for $\alpha = n$ and $\beta = -n$. Denote each of these elements by W_{ij} such that

$$\langle nn|H'|n(-n)\rangle = \begin{pmatrix} W_{nn} & W_{n(-n)} \\ W_{(-n)n} & W_{(-n)(-n)} \end{pmatrix} \tag{1}$$

Getting the eigenvalues of this matrix, we get the first-order energy correction as

$$E^1_{\pm} = \frac{1}{2}\left[(W_{nn} + W_{(-n)(-n)}) \pm \sqrt{(W_{nn} + W_{(-n)(-n)})^2 - 4(W_{nn}W_{(-n)(-n)} - |W_{ab}|^2)}\right] \tag{2}$$

Now we calculate each of the elements using $W_{ij} = \int \psi_i^*(x) H' \psi_j(x) dx$:

$$\begin{aligned} W_{nn} = W_{(-n)(-n)} &= \frac{V_0}{L}\int_{-L/2}^{L/2} \exp\left(-\frac{x^2}{a^2}\right) dx \\ &= \frac{V_0}{L}\int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{a^2}\right) dx = \frac{V_0}{L}\sqrt{\frac{\pi}{1/a^2}} = V_0\sqrt{\pi}\frac{a}{L} \end{aligned} \tag{3}$$

where we did a slight trick: extending the bounds of integration. This is valid for the approximation $a << L$, since a Gaussian function technically have small tails for which there's negligible contribution if we are to compute the integral (cf. 68-95-99.7 rule for 1-2-3σ). The rest is straightforward. Using the same trick, as well as the Gaussian integral $\int_{-\infty}^{\infty} \exp(-\alpha x^2 + \beta x + \gamma) dx = \sqrt{\dfrac{\pi}{\alpha}} \exp(\beta^2/4\alpha + \gamma)$ for $\alpha = 1/a^2$, $\beta = \pm 4\pi i n/L$, and $\gamma = 0$,

$$\begin{aligned} W_{n(-n)} &= \frac{V_0}{L}\int_{-\infty}^{\infty} \exp\left(-\frac{4\pi i n x}{L}\right) \exp\left(-\frac{x^2}{a^2}\right) dx \\ &= \frac{V_0}{L} a\sqrt{\pi} \exp\left(-4\pi^2 n^2 \frac{a^2}{L^2}\right) \end{aligned} \tag{4}$$

and

$$W_{(-n)n} = \frac{V_0}{L}\int_{-\infty}^{\infty} \exp\left(\frac{4\pi inx}{L}\right)\exp\left(-\frac{x^2}{a^2}\right)dx$$
$$= V_0\frac{a}{L}\sqrt{\pi}\exp\left(4\pi^2n^2\frac{a^2}{L^2}\right) \tag{5}$$

Then we make an approximation: since $a << L$, we can effectively get rid of the extra exponential terms. Then, substituting to equation (2),

$$E^1_\pm = \frac{1}{2}\left[V_0\sqrt{\pi}\frac{a}{L} + V_0\sqrt{\pi}\frac{a}{L} \pm \sqrt{(V_0\sqrt{\pi}\frac{a}{L} + V_0\sqrt{\pi}\frac{a}{L})^2 - 4(V_0\sqrt{\pi}\frac{a}{L}V_0\sqrt{\pi}\frac{a}{L} - |V_0\sqrt{\pi}\frac{a}{L}|^2)}\right]$$
$$E^1_+ = 2V_0\sqrt{\pi}\frac{a}{L} \tag{6}$$
$$E^1_- = 0 \tag{7}$$

We can now diagonalize the perturbation matrix. To do this, we find the coefficients to a general combination of $|\psi_n\rangle$ and $|\psi_{-n}\rangle$, say $\alpha\psi_n + \beta\psi_{-n}$. For E^1_-,

$$\frac{V_0}{L}\int(\alpha\psi_n + \beta\psi_{-n})^*\exp\left(-\frac{x^2}{a^2}\right)(\alpha\psi_n + \beta\psi_{-n})\,dx = V_0\frac{a}{L}\sqrt{\pi}(\alpha^2 + 2\alpha\beta + \beta^2) \tag{8}$$
$$= V_0\frac{a}{L}\sqrt{\pi}(\alpha+\beta)^2 \tag{9}$$

Then we apply this to E^1_+:

$$V_0\frac{a}{L}\sqrt{\pi}(\alpha+\beta)^2 = 2V_0\sqrt{\pi}\frac{a}{L}$$
$$\longrightarrow \alpha + \beta = \sqrt{2} \tag{10}$$

Normalizing this, we get $\alpha = \frac{1}{\sqrt{2}}$ and $\beta = -\frac{1}{\sqrt{2}}$ for E^1_-. For E^1_+, we plug $\alpha = \sqrt{2} - \beta$ back to the normalization condition so that $\alpha = \beta = \frac{1}{\sqrt{2}}$. Thus our final wavefunctions are

$$\frac{\psi_n(x) + \psi_{-n}(x)}{\sqrt{2}} = \frac{1}{\sqrt{2L}}\exp\left(2\pi in\frac{x}{L}\right) + \frac{1}{\sqrt{2L}}\exp\left(-2\pi in\frac{x}{L}\right) = \sqrt{\frac{2}{L}}\cos\left(2\pi n\frac{x}{L}\right) \tag{11}$$
$$\frac{\psi_n(x) -_{-n}(x)}{\sqrt{2}}\frac{1}{\sqrt{2L}}\exp\left(2\pi in\frac{x}{L}\right) - \frac{1}{\sqrt{2L}}\exp\left(-2\pi in\frac{x}{L}\right) = \sqrt{\frac{2}{L}}\sin\left(2\pi n\frac{x}{L}\right). \tag{12}$$

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Problem 2

VARIATIONAL METHOD. To use the variational method for approximating the ground state energy of an electron in a hydrogen atom, we pick a trial Gaussian wavefunction of the form

$$|\psi, \alpha\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\alpha\frac{r^2}{2}\right) \tag{1}$$

which is already normalized. This trial wavefunction is a function of α. We then calculate the matrix elements of H, which makes the basis for our trial energy $E(\alpha)$. We then minimize this with respect to α to get the minimal energy which can be used as an approximation to the exact ground state energy.

To do this, we first let $a_0 = \dfrac{\hbar^2}{2m_e e^2}$ be the Bohr radius in Gaussian units. Then, we write the Hamiltonian of the hydrogen atom in Gaussian units too:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} = -e^2\left(\frac{a_0}{2}\nabla^2 + \frac{1}{r}\right) \tag{2}$$

We make this act on $|\psi, \alpha\rangle$, giving

$$\begin{aligned} H|\psi, \alpha\rangle &= \left[-e^2\left(\frac{a_0}{2}\nabla^2 + \frac{1}{r}\right)\right]\left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\alpha\frac{r^2}{2}\right) && (3)\\ &= -e^2\left(\frac{\alpha}{\pi}\right)^{1/4}\left[\frac{a_0}{2}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\exp\left(-\alpha\frac{r^2}{2}\right)\right)\right) + \frac{1}{r}\exp\left(-\alpha\frac{r^2}{2}\right)\right] && (4)\\ &= -e^2\left(\frac{\alpha}{\pi}\right)^{1/4}\left[\frac{a_0}{2}\alpha^2(r^2\alpha - 3) + \frac{1}{r}\right]\exp\left(-\alpha\frac{r^2}{2}\right) && (5) \end{aligned}$$

We see that the only Laplacian terms that survive are the radial operators, which is easy to see from the radial Gaussian wavefunction Then, by making a bra act on this new ket, we complete the matrix elements. We then integrate this with respect to r, noting that we are doing a spherical coordinate integration so that we need to include scale factors $4\pi r^2$.

We first recall some important Gaussian integrals:

$$\begin{aligned} \int_0^\infty r\exp(-\alpha r^2)\,dr &= \frac{1}{2} && (6)\\ \int_0^\infty r^2\exp(-\alpha r^2)\,dr &= -\frac{\partial}{\partial\alpha}\int_0^\infty \exp(-\alpha r^2)\,dr = \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} && (7)\\ \int_0^\infty r^4\exp(-\alpha r^2)\,dr &= \frac{\partial^2}{\partial\alpha^2}\int_0^\infty \exp(-\alpha r^2)\,dr = -\frac{3}{8\alpha^2}\sqrt{\frac{\pi}{\alpha}} && (8) \end{aligned}$$

Thus, we have

$$\langle \psi, \alpha | H | \psi, \alpha \rangle = -4\pi e^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^\infty dr\ r^2 \left[\frac{a_0}{2}\alpha^2(r^2\alpha - 3) + \frac{1}{r}\right] \exp\left(-\alpha r^2\right) \tag{9}$$

$$= 4\pi e^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^\infty r^2 \exp\big(-\alpha r^2\big) \left[\frac{3}{2}a_0\alpha^2 - \frac{a_0}{2}\alpha^3 r^2 - \frac{1}{r}\right] \tag{10}$$

$$E(\alpha) = 4\pi e^2 \left[\frac{9}{16}a_0\alpha - \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right] \tag{11}$$

We then proceed to differentiate this expression wrt α then set it to zero:

$$\frac{\partial}{\partial \alpha}(11) = \frac{9}{16}(4\pi e^2)a_0 - \frac{1}{2\sqrt{\pi}}(4\pi e^2)\left(-\frac{1}{2}\alpha^{-1/2}\right) = 0 \tag{12}$$

$$\longrightarrow \alpha_{\min} = \frac{16}{81\pi a_0^2} \tag{13}$$

Thus we have $E_{\min} = E(\alpha_{\min}) = -\dfrac{e^2}{9\pi a_0}$. Comparing with the value of $E_0 = -\dfrac{e^2}{2a_0}$ from Appendix A6 of Sakurai, we have

$$\boxed{\frac{E_{\min}}{E_0} = \frac{2}{9\pi} \approx 0.07} \tag{14}$$

We also compare α with the standard deviation σ of a Gaussian PDF. Recall that

$$\mathcal{N}(x; \mu, \sigma) = C \exp\big(-(x-\mu)^2/2\sigma^2\big) \tag{15}$$

so that for our trial Gaussian wavefunction, $\sigma = \dfrac{1}{\sqrt{\alpha}} = \dfrac{9}{4}\sqrt{\pi}a_0$. Comparing this with the Bohr radius, we get

$$\boxed{\frac{\sigma}{a_0} = \frac{9}{4}\sqrt{\pi} \approx 4.0} \tag{16}$$

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