Problem 1

Kramers degeneracy. In this problem, we are basically asked to prove the existence of Kramers degeneracy.

(a) Consider an energy eigenket $|n\rangle$. Being an energy eigenket means it satisfies $\hat{H}|n\rangle = E_n|n\rangle$, for which E_n is nondegenerate. Next, consider it being time-reversal invariant, so that it satisfies $\Theta|n\rangle = e^{i\alpha}|n\rangle$ as well. This means that the two operators $\hat{H}$ and Θ commute, and that $|n\rangle$ and $\Theta|n\rangle$ have the same energy eigenvalue E_n. If the system then has a half-integer spin j_{odd} (say a system with an odd number of electrons), then by the action of the time reversal operator on spins,

$$\Theta^2|j_{\text{odd}}\rangle = -|j_{\text{odd}}\rangle \tag{1}$$

due to the double-valued representation of the classical rotations for the case of the half-integer angular momentum, which is a result of using the UK decomposition of Θ. Applying this to $|n\rangle$, we conclude that $\Theta^2|n\rangle = \Theta(\Theta|n\rangle) = -|n\rangle$.

We then arrive at an inconsistency: E_n cannot be nondegenerate if it's meant to satisfy $\Theta|n\rangle$ as well. Thus we have energy levels of at least two-fold degeneracy (which is assured to be even due to the structure of the Θ-invariant subspace).

(b) To remove this degneracy, we need a Hamiltonian that doesn't commute with the time operator Θ.

Recall the Hamiltonian of a system in an external electric field with potential Φ:

$$\hat{H} = \frac{\hat{p}^2}{2m} + q\Phi \tag{2}$$

for which when we apply time reversal leaves the Hamiltonian invariant, since $\hat{p}$ changes signs under conjugation with Θ while Φ does not. However, if we put the system in an external magnetic field, the Hamiltonian becomes

$$\hat{H} = \frac{1}{2m}\left[\hat{p} - \frac{q}{c}\hat{\mathbf{A}}\right]^2 \tag{3}$$

for which $\hat{\mathbf{A}}$ does not change signs under time reversal, which does not make the Hamiltonian invariant under time reversal.

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Problem 2

Van der Waals Interaction. In this problem, we show how the time-independent perturbation theory allows us to explore properties of the interaction forces between hydrogen atoms, particularly the Van der Waals interaction.

Consider the configuration shown on figure 1.

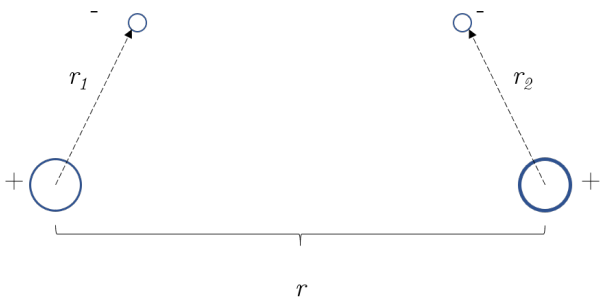

Figure 1: Setting up two hydrogen atoms with the same spin at a distance $r >> a_0$ measured between their protons. At this distance, their electron clouds would not overlap, and only the Van der Waals interaction is present.

Since we set the atoms up such that the wave functions of their electrons would not overlap, we can safely say that there is no chemical bond present. If the spin of the two atoms are the same, only the Van der Waals would be present in terms of attractive interactions.

To use the Rayleigh-Schrodinger perturbation theory on this configuration, we first expand the Hamiltonian in terms of the zeroth-order H_0 and interaction terms H':

$$H = H_0 + H', \tag{1}$$

$$H_0 = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \tag{2}$$

$$H' = \frac{e^2}{r} + \frac{e^2}{|(\mathbf{r} + \mathbf{r}_2) - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r} + \mathbf{r}_2|} - \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} \tag{3}$$

where we listed all the interactions between the protons themselves and the proton-electron interactions. Since we can separate the wavefunctions in the H_0 solution in terms of the different r_1 and r_2, we can write the solution to $H_0U_0 = E_0U_0$ as product eigenstates in the ground state:

$$U_0 = U_{100}(r_1)U_{100}(r_2) \tag{4}$$

having an energy eigenvalue $E_0 = -2E_I$ for the whole system, where E_I is the ionization energy of one hydrogen atom. We can then treat H' as a perturbation for which we can

expand each of the distances in the denominators asymptotically, in terms of r_1/r or r_2/r, using the general multipole expansion. For example,

$$\frac{e^2}{|\mathbf{r}+\mathbf{r}_2|} = \frac{1}{r}\sum_{\ell=0}^{\infty}\left(\frac{e^2}{r^3}\right)^{\ell} P_\ell(\cos\alpha_2) \tag{5}$$

$$= \frac{e^2}{r} + \frac{e^2(\mathbf{r}\cdot\mathbf{r}_2)}{r^3} + \mathcal{O}\left(\frac{e^2}{r^4}\right) \tag{6}$$

Here, we only include the dipole-dipole term which is the leading term in the perturbation. We do that to the other two terms, cancelling the first term, such that

$$\frac{e^2}{|\mathbf{r}+\mathbf{r}_2-\mathbf{r}_1|} = \frac{e^2}{r} + \frac{e^2(\mathbf{r}\cdot\mathbf{r}_2+\mathbf{r}_1)}{r^3} + \mathcal{O}\left(\frac{e^2}{r^4}\right) \tag{7}$$

$$\frac{e^2}{|\mathbf{r}-\mathbf{r}_1|} = \frac{e^2}{r} - \frac{e^2(\mathbf{r}\cdot\mathbf{r}_1)}{r^3}\mathcal{O}\left(\frac{e^2}{r^4}\right) \tag{8}$$

Simplifying and retaining only dipole-dipole contributions,

$$H'_{dd} = \frac{e^2}{r^3}(x_1x_2 + y_1y_2 - 2z_1z_2) \tag{9}$$

Now we can calculate the first and second order perturbations: for the first-order,

$$W_1 = \frac{e^2}{r^3}\langle 100|x_1x_2 + y_1y_2 - 2z_1z_2|100\rangle \tag{10}$$

$$= \frac{e^2}{r^3}\iint dr_1^3 dr_2^3\; U_{100}^2(r_1)U_{100}^2(r_2)(x_1x_2 + y_1y_2 - 2z_1z_2) \tag{11}$$

Here we see that the Hamiltonian perturbation (9) is an odd function of each coordinate ($\ell < 0$), while U_{100} is even ($\ell = 0$), thus making the integral vanish ($\int Y_\ell^m(\Omega)\; d\Omega = 0$), even for higher order terms of H' (which also contains $\ell > 0$ terms).

For the second-order perturbation,

$$W_2 = \sum_{n_1\neq 1}\sum_{\ell_1}\sum_{m_1}\sum_{n_2\neq 1}\sum_{\ell_2}\sum_{m_2}\frac{|\langle 100|\,\langle 100|H'_{dd}|n_1\ell_1m_1\rangle\,|n_2\ell_2m_2\rangle\,|^2}{E_0 - E_1 - E_2} \tag{12}$$

$$= \frac{e^4}{r^6}\sum_{k\neq 0}\frac{|\langle k^{(0)}|x_1x_2 + y_1y_2 - 2z_1z_2|0^{(0)}\rangle\,|^2}{E_0 - E_1 - E_2} \tag{13}$$

for which we see the $1/r^6$ dependence of the perturbation, which is the description for the Van der Waals interaction.

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Problem 3

Perturbed Harmonic Oscillator. In this problem, we consider a harmonic oscillator parametrized by its natural frequency ω to be perturbed by a weak constant force $f > 0$.

To use time-independent perturbation theory, we recall that the Hamiltonian must have a perturbation $H = H_0 + H'$ where $H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$ and H' is related ot the constant force perturbation. We then derive the contribution of the constant force to the perturbation from $F(x) = -\frac{dV}{dx}$ so that $V(x) = -fx$ for some positive constant force, which we consider to be H' as well.

(a) We first solve the shift in energy levels, particularly the ground state. In general, the first order correction can be classified as

$$E_0^{(1)} = \langle 0|H'|0\rangle = -f\langle 0|x|0\rangle \tag{1}$$

Since $x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$, making it act on the ground state wavefunction makes the whole thing vanish (because there's no state lower than $|0\rangle$ and $\langle 0|1\rangle = 0$), so $\boxed{E_0^{(1)} = 0}$.

The second order correction follows from the formula

$$E_0^{(2)} = \sum_{n'\neq 0} \frac{|\langle n'|H'|0\rangle|^2}{E_0 - E_n'} \tag{2}$$

$$\langle n'|H'|0\rangle = -f\langle n'|x|0\rangle = -f\sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\langle n'|1\rangle) \tag{3}$$

so that the only contribution will come from $n' = 1$, yielding a second-order correction to the energy term $\boxed{E_0^{(2)} = -\frac{f^2}{2m\omega^2}}$, or $\boxed{E_0' = \frac{1}{2}\hbar\omega - \frac{f^2}{2m\omega^2}}$.

(b) We can also complete the square of the Hamiltonian $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 - fx$:

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - fx = \frac{p^2}{2m} + \frac{1}{2}m\omega^2\left(x^2 - \frac{2f}{m\omega^2}x + \frac{f^2}{m^2\omega^4}\right) - \frac{f^2}{2m\omega^2} \tag{4}$$

$$H^*(x') = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x'^2 - \frac{f^2}{2m\omega^2} \tag{5}$$

which we can apply to some $\psi(x')$, $x' = x - \frac{f}{m\omega^2}$ that allows us to do the following:

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$$H^* |0\rangle = E_0^* |0\rangle \rightarrow \left(\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x'^2 \right) |0\rangle - \frac{f^2}{2m\omega^2} |0\rangle \quad = E_0^* |0\rangle \tag{6}$$

$$\left(\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x'^2 \right) |0\rangle = \left(E_0^* + \frac{f^2}{2m\omega^2} \right) |0\rangle \tag{7}$$

$$\frac{1}{2}\hbar\omega |0\rangle = \left(E_0^* + \frac{f^2}{m\omega^2} \right) |0\rangle \tag{8}$$

so that $\boxed{E_0^* = \frac{1}{2}\hbar\omega - \frac{f^2}{2m\omega^2}}$ is the exact ground state energy, cf. E_0' solved earlier.

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Problem 4

Delta Function Perturbation. In this problem, we consider a repulsive delta function potential $H' = \alpha\delta(x - a/2)$ located at the center of an infinite square well of length a. Since the delta potential is repulsive, we are sure that $\alpha > 0$.

We first recall the ground state energy for a plain infinite square well: $E_1 = \dfrac{\pi^2\hbar^2}{2ma^2}$. We use non-degenerate perturbation theory to calculate the shift in E_1 up to second-order. In the first order, we use

$$E_1^1 = \left\langle \psi_1^0 \middle| H' \middle| \psi_1^0 \right\rangle \tag{1}$$

where $\psi_1^0(x) = \langle x|\psi_1^0\rangle = \sqrt{\dfrac{2}{a}} \sin\dfrac{\pi x}{a}$ is the unperturbed ground state wavefunction. We then solve for equation (1) using the expansion in x-basis:

$$E_1^1 = \left\langle \psi_1^0 \middle| \alpha\delta(x - a/2) \middle| \psi_1^0 \right\rangle = \alpha \int_0^\infty (\psi_1^0(x))^2 \delta(x - a/2)dx \tag{2}$$

$$= \frac{2\alpha}{a} \sin^2\frac{\pi}{2} = \frac{2}{a}\alpha \tag{3}$$

For the second order contribution, we use $E_1^2 = \sum_{m\neq 1} \dfrac{|\langle\psi_m^0|H'|\psi_1^0\rangle|^2}{E_1^0 - E_m^0}$. We first simplify the denominator as follows:

$$E_1^2 = \sum_{m\neq 1} \frac{|\langle\psi_m^0|H'|\psi_1^0\rangle|^2}{\dfrac{\pi^2\hbar^2}{2ma^2} - \dfrac{m^2\pi^2\hbar^2}{2ma^2}} \tag{4}$$

$$= \frac{2ma^2}{\pi^2\hbar^2} \sum_{m\neq 1} \frac{|\langle\psi_m^0|H'|\psi_1^0\rangle|^2}{1 - m^2} \tag{5}$$

Now we calculate for the matrix elements. As before, we use the integral expansion in x-basis:

$$\left\langle \psi_m^0 \middle| H' \middle| \psi_1^0 \right\rangle = \frac{2\alpha}{a} \int_0^\infty \sin\frac{m\pi x}{a} \delta(x - a/2) \sin\frac{\pi x}{a} dx \tag{6}$$

$$= \frac{2\alpha}{a} \sin\frac{m\pi}{2} \sin\frac{\pi}{2} \tag{7}$$

Thus, the second order correction can be written as

$$E_1^2 = \frac{2ma^2}{\pi^2\hbar^2}\frac{4\alpha^2}{a^2}\sum_{m\neq 1}\frac{\sin^2\frac{m\pi}{2}}{1-m^2} \tag{8}$$

$$= \frac{8m\alpha^2}{\pi^2\hbar^2}\sum_{m\neq 1}\frac{1}{1-m^2} \tag{9}$$

$$= \frac{8m\alpha^2}{\pi^2\hbar^2}\left(1-\frac{1}{3}-\frac{1}{8}-\frac{1}{15}-\dots\right) \tag{10}$$

$$= \frac{8m\alpha^2}{\pi^2\hbar^2}\left(-\frac{1}{4}\right) = \frac{-2m\alpha^2}{\pi^2\hbar^2} \tag{11}$$

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