B7.3 Further Quantum Theory

Problem Sheet 3

Hilary Term 2020

`[Last update: 23:57 on Wednesday 19th February, 2020]`

On this problem sheet, the first three problems (on perturbation theory) are to be turned in for marking. The last problem is on variational methods, which we will probably not discuss until very close to the homework deadline. You should nevertheless try to solve the last problem for discussion in class.

3.1 Anharmonic oscillator

In lectures we encountered the one-dimensional *anharmonic oscillator*, with Hamiltonian given by

$$H_{\text{AHO}} = \frac{P^2}{2m} + \frac{m\omega^2}{2}X^2 + \lambda\frac{m^2\omega^3}{\hbar}X^4 \ , \qquad \lambda \ll 1 \ .$$

We derived the leading perturbative correction in λ to the ground state energy and announced the result for the state itself, namely

$$E_0' = \tfrac{3}{4}\hbar\omega \ , \qquad \psi_0' = -\tfrac{3}{2^{3/2}}\psi_2 - \tfrac{3^{1/2}}{2^{5/2}}\psi_4 \ .$$

(*i*) Re-derive the above results in detail. You should, of course, use the formalism of ladder operators $\alpha_\pm$ as on problem sheet 1. Don't do any integrals!

(*ii*) Now find the general result for the first-order corrections E_n' and ψ_n' for general $n > 0$. This could get messy fast, so you will probably want to think of a good way to organize your calculations. It might help to remember that $\alpha_+\alpha_- = N$ acts according to $N\psi_n = n\psi_n$.

Now consider the *two-dimensional* harmonic oscillator perturbed by an anharmonic coupling,

$$H_{\text{AHO}_{2d}} = \frac{P_1^2 + P_2^2}{2m} + \frac{1}{2}m\omega^2(X_1^2 + X_2^2) + \lambda\frac{m^2\omega^3}{\hbar}X_1^2X_2^2 \ , \qquad \lambda \ll 1 \ .$$

In this case the unperturbed system has non-trivial degeneracy for each energy level other than the ground state.

(*iii*) Compute the corrections to the ground state energy and wavefunction to first order in λ using non-degenerate perturbation theory.

(*iv*) Now find the first-order corrections to the second, third, and fourth energy levels. (These are degenerate levels, so you need to implement first-order degenerate perturbation theory and find how the previously degenerate states are split). Observe how much degeneracy persists at these levels to this order. Can you explain some or all of this remaining degeneracy using discrete symmetries of the Hamiltonian?

3.2 Fine structure of the Hydrogen atom

There are three *fine-structure* corrections to the Hydrogen atom Hamiltonian are the relativistic kinetic energy term, the spin-orbit coupling term, and the "Darwin" term,

$$\begin{aligned} H'_{\text{KE}} &= \frac{-P^4}{8m_e^3c^2} \ , \\ H'_{\text{SO}} &= \frac{e^2}{2m_e^2c^2}\frac{\mathbf{L}\cdot\mathbf{S}}{r^3} \ , \\ H'_{\text{Dar}} &= \frac{\pi\hbar^2e^2}{2m_e^2c^2}\delta^3(\mathbf{r}) \ . \end{aligned}$$

In lectures we looked at the first-order corrections to the energy spectrum due to the spin-orbit term, which are given by

$$E'_{nlj} = \frac{nE_n^2}{m_e c^2}\left(\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)}\right) .$$

In this exercise you will confirm this expression, and perform some of the integrals that were too pesky to do on the board. You will also compute the comparable corrections coming from the relativistic kinetic energy correction and the Darwin term.

(*i*) Using degenerate first-order perturbation theory, explain carefully why we can compute the first-order corrections to the Hydrogen atom energy levels by evaluating

$$E'_{nlj} = \langle \psi^m_{nlj} | H'_{\text{KE}} + H'_{\text{SO}} + H'_{\text{Dar}} | \psi^m_{nlj} \rangle ,$$

where ψ^m_{nlj} is the Hydrogen stationary state in the total-angular momentum basis (*i.e.*, diagonalizing J^2, L^2, S^2, and J_3).

(*ii*) Compute the leading correction to the energy eigenvalues due to the relativistic kinetic term. For this you should use that $P^2 = 2m_e H + 2m_e e^2/r$, which you can use to show that

$$\left\langle \frac{P^4}{8m_e^3 c^2} \right\rangle_{\psi^m_{nlj}} = \frac{E_n^2}{2m_e c^2} + \frac{E_n}{m_e c^2}\left\langle \frac{e^2}{r} \right\rangle_{nl} + \frac{1}{2m_e c^2}\left\langle \frac{e^4}{r^2} \right\rangle_{nl} ,$$

where the expectation values on the right-hand side are computed using just the radial wavefunctions $R_{nl}(r)$ that only depend on the principal and orbital angular momentum quantum numbers. You can use the results[1]

$$\left\langle \frac{e^2}{r} \right\rangle_{nl} = 2E_n , \qquad \left\langle \frac{e^4}{r^2} \right\rangle_{nl} = \frac{4nE_n^2}{l+\frac{1}{2}} .$$

(*iii*) Re-derive the expression above (and from lecture) for the energy shifts due to spin-orbit coupling. For this calculation, it is important to be able to evaluate the radial integral[2]

$$\left\langle \frac{1}{r^3} \right\rangle_{n,l} = \frac{1}{n^3 a^3}\frac{1}{l(l+\frac{1}{2})(l+1)} .$$

(*iv*) Now compute the contribution due to the Darwin term. You will recall that due to the centrifugal term in the effective radial Schrödinger equation for the Hydrogen atom, only the wavefunctions of the $l = 0$ states are non-vanishing at the origin. For these wave-functions one has (*cf.* Eqn. (3.7.58) of Sakurai where $Y_0^0(\theta, \phi) = (4\pi)^{-\frac{1}{2}}$):

$$R_{n0}(0) = \frac{1}{a^{\frac{3}{2}} n^{\frac{3}{2}} \pi^{\frac{1}{2}}} .$$

Taking all of the fine-structure corrections together, your final result for the shifted Hydrogen energy levels should take the surprisingly simple form,

$$E'_n = \frac{nE_n^2}{m_e c^2}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) .$$

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[1] Though, really, you should try to derive these expressions for the relevant radial integrals. For the first, recall that for the Hydrogen-like atom with atomic number Z, one has

$$\langle \psi^j_{nlm}(Z) | H(Z) | \psi^j_{nlm}(Z) \rangle = Z^2 E_n(0) .$$

Differentiating with respect to Z and evaluating at $Z = 1$ allows you to compute $\langle r^{-1} \rangle$. A similar trick can be used to compute $\langle r^{-2} \rangle$, but you have to pass to the effective radial quantum mechanics and remember that in the derivation of the hydrogen atom, $n = l + k$ where $k - 1$ is the degree of the polynomial appearing in the radial wavefunction.

[2] For a bonus, you can derive this result using the following strategy: First, define the "radial momentum" operator $P_r = -i\hbar(\partial_r + r^{-1})$. Note that the radial component of the kinetic term in the spherical Schrödinger equation is given by $\frac{\hbar^2}{2m}P_r^2$. Then show that in any energy eigenstate ψ and for any operator A, one has $\langle \psi | [A, H] | \psi \rangle = 0$. Thus, setting $A = P_r$, conclude that

$$e^2 \left\langle \frac{1}{r^2} \right\rangle - \frac{1}{m_e}\left\langle \frac{L^2}{r^3} \right\rangle = 0 ,$$

and thus, using the results of part (*i*), deduce the formula of interest.

Perhaps the most surprising thing is that the l-dependence has cancelled out and the corrections are completely controlled by the total angular momentum quantum number j. A much more transparent derivation of this result proceeds using the relativistic *Dirac equation.*

3.3 Degenerate perturbation theory at second order

In the case of a degenerate energy level, the first-order corrections to the corresponding eigenstates are given by

$$|\psi_k'\rangle = \sum_{m:E_m\neq E_k} \frac{\langle\psi_m|H'|\psi_k\rangle}{E_k - E_m}\psi_m + \sum_{\substack{r:E_r=E_k\\ \psi_r\perp\psi_k}} \lambda_r\psi_r ,$$

where ψ_k is chosen to diagonalize the restriction of H' to the degenerate eigenspace.

(*i*) By formulating an appropriate solvability criterion for the *second-order* correction to the eigenstate, ψ_k'', find an expression for the coefficients λ_r. Under what conditions does your answer determine the coefficients?

(*ii*) Apply your result to the analysis of the *third energy level* (unperturbed energy $E = 3\hbar\omega$) of the anharmonically coupled oscillators from problem **3.1**. Which perturbed states can you now determine unambiguously at first order?

3.4 Variational Method

We want to explore the application of the variational method in a few examples. In each case below, use the variational Ansatz given to estimate the ground state energy of the stated system.

(*i*) Harmonic oscillator (with potential $V(x) = \frac{1}{2}m\omega^2X^2$) with variational Ansatz $\psi_\alpha(x) \sim \exp(-\alpha x^2)$.

(*ii*) Harmonic oscillator with variational Ansatz $\psi_a(x) \sim \frac{1}{x^2+a^2}$. Not every Ansatz is a good one!

(*iii*) Particle in a box (the interval $-a \leqslant x \leqslant a$) with trial functions $\psi_n(x) \sim (a^2 - x^2)^n$ for $n = 1, 2, 3$. These will give you a few upper bounds on the ground state energy. Compare to the exact answer. If you are interested and adventurous, try to consider the case $\psi_\lambda(x) \sim (a^2 - x^2)^\lambda$ for continuous λ and optimize. You can get to within .3% of the exact answer this way!

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