Moderne Theoretische Physik I
Grundlagen der Quantenmechanik

Summer Semester 2024
Exercise Sheet 12

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Due date: 19. 07. 2024.

The problems whose solutions you need to upload are designated with stars.

⋆ Problem 1 ⋆ Anharmonic oscillator

Consider an anharmonic oscillator of the form

$$H = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 + \alpha\hat{x}^4 \tag{1}$$

where the third term can be considered as a perturbation $\alpha x_0^4 \ll \hbar\omega$. Here $x_0 = \sqrt{\frac{\hbar}{m\omega}}$ is the characteristic length scale of the simple harmonic oscillator. For $\alpha = 0$, the problem is exactly solvable, where the energies of the states $\{|n\rangle\}$ for $n \in N_0$ are given by $E_n^{(0)} = \hbar\omega(n + \frac{1}{2})$. It was shown that ascending and descending operators

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left[\hat{x} + \frac{i}{m\omega}\hat{p}\right], \tag{2}$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left[\hat{x} - \frac{i}{m\omega}\hat{p}\right] \tag{3}$$

whose effect on states is given by

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \tag{4}$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{5}$$

The first correction to the state energy is

$$E_n^{(1)} = \alpha\langle n|\hat{x}^4|n\rangle. \tag{6}$$

1. Calculate the matrix element $\langle n|\hat{x}^2|n'\rangle$. Show that $n' = n, n \pm 2$ must hold to have non-zero value.
2. Compute $E_n^{(1)}$ to first order in α. (Hint: The identity operator is given by $\hat{1} = \sum_n |n\rangle\langle n|$.)
3. Derive an expression for $n = n_{max}$ for which the perturbation theory is no longer valid. One possible criterion is

$$E_{n_{max}}^{(0)} \approx E_{n_{max}}^{(1)} \tag{7}$$

Solution 1

1. First, $\hat{x}$ is expressed by $\hat{a}$ and $\hat{a}^\dagger$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a}) \tag{8}$$

   This follows

$$\hat{x}^2 = \frac{x_0^2}{2}(\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}\hat{a}) \tag{9}$$

   The ascending and descending operators increase or decrease the index l.

$$\hat{a}^\dagger\hat{a}^\dagger|l\rangle = \sqrt{l+1}\sqrt{l+2}|l+2\rangle, \tag{10}$$
$$\hat{a}^\dagger\hat{a}|l\rangle = l|l\rangle, \tag{11}$$
$$\hat{a}\hat{a}^\dagger|l\rangle = (l+1)|l\rangle, \tag{12}$$
$$\hat{a}\hat{a}|l\rangle = \sqrt{l}\sqrt{l-1}|l-2\rangle \tag{13}$$

   In order for the matrix elements to be non-zero, the following must apply: $\langle n|l \pm (0,2)\rangle = \delta_{n,(l\pm(0,2))}$. This means that only states with $l = n, n \pm 2$ contribute.

2. The expected value can be written by inserting $\hat{1} = \sum_l |l\rangle\langle l|$ as

$$\begin{aligned}\alpha\langle n|\hat{x}^4|n\rangle &= \alpha\sum_l \langle n|\hat{x}^2|l\rangle\langle l|\hat{x}^2|n\rangle = \alpha\sum_l |\langle n|\hat{x}^2|l\rangle|^2 \\ &= \frac{\alpha x_0^4}{4}\sum_l \Big((l+1)(l+2)|\langle n|l+2\rangle|^2 + (2l+1)^2|\langle n|l\rangle|^2 + l(l-1)|\langle n|l-2\rangle|^2\Big) \\ &= \frac{\alpha x_0^4}{4}(3 + 6n + 6n^2)\end{aligned} \tag{14}$$

   This results in

$$E_n^{(1)} = \frac{\alpha x_0^4}{4}(3 + 6n + 6n^2). \tag{15}$$

3. It can be seen that $E_n^{(1)}$ grows quadratically with n, whereas $E_n^{(0)}$ only grows linearly. Thus the approximation fails for large n. One can assume that the maximum value for n is given by

$$E_{n_{max}}^{(0)} \approx E_{n_{max}}^{(1)} \tag{16}$$

   for $n_{max} \gg 1$. Therefore

$$\hbar\omega n_{max} \approx \frac{3\alpha x_0^4}{2}n_{max}^2 \Rightarrow n_{max} \approx \frac{2}{3}\frac{\hbar\omega}{\alpha x_0^4}. \tag{17}$$

   Thus, the result of the perturbation calculation is meaningful for $n \ll n_{max} \approx \frac{2}{3}\frac{\hbar\omega}{\alpha x_0^4}$.

⋆ Problem 2 ⋆ Schmidt decomposition and reduced density matrices

Consider a bipartite quantum system built from a direct product Hilbert space of the two parts, $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$. Let $|a_i\rangle_A$ with $i = 1, 2, \cdots n$ label a complete orthonormal basis of states in Hilbert space A, and likewise for Hilbert space B: $|b_j\rangle_B$, with $j = 1, 2, \cdots N \geq n$. The most general quantum state in the full Hilbert space can be expressed as,

$$|\Phi\rangle = \sum_{n=1}^{n}\sum_{j=1}^{N} c_{ij}|a_i\rangle_A \otimes |b_j\rangle_B, \tag{18}$$

with complex coefficients, c_{ij}.

A theorem proven on the wikipedia page, https://en.wikipedia.org/wiki/Schmidt_decomposition, states that there always exist orthonormal sets, $|\psi_i\rangle_A$, $|\phi_j\rangle_B$ with $i, j = 1, 2, \cdots n$ such that the general state $|\Phi\rangle$ can be re-expressed in a Schmidt-decomposed form:

$$|\Phi\rangle = \sum_i^n v_i |\psi_i\rangle_A \otimes |\phi_i\rangle_B \tag{19}$$

with the normalization condition, $\sum_{i=1}^n |v_i|^2 = 1$.

1. Using this Schmidt form, obtain expressions for the reduced density matrices,

$$\hat{\rho}_A = Tr_B|\Phi\rangle\langle\Phi|, \quad \hat{\rho}_B = Tr_A|\Phi\rangle\langle\Phi| \tag{20}$$

Demonstrate that the reduced density matrices are Hermitian with eigenvalues $\lambda_i = |v_i|^2$, $i = 1, 2, \cdots n$, and associated eigenvectors, $|\psi_i\rangle_A$, $|\phi_i\rangle_B$. Thus, the Schmidt-decomposition for any state $|\Phi\rangle$ can be obtained by computing and then diagonalizing the reduced density matrices.

2. Now consider, as an example, two spin-$\frac{1}{2}$ particles, labelled A and B, in a (normalized) pure state,

$$|\Phi\rangle = \frac{1}{\sqrt{2}}|\downarrow\rangle_A \otimes |\downarrow\rangle_B + \frac{1}{2}|\uparrow\rangle_A \otimes (|\uparrow\rangle_B + |\downarrow\rangle_B). \tag{21}$$

Obtain the Schmidt-decomposition of this state by computing and diagonalizing the two reduced density matrices and show that the expression of $|\Phi\rangle$ obtained from Eq. (19) is same to the Eq. (21).

Solution 2

1. We can always extend the orthonormal set $\{|\phi_j\rangle_B\}_{j=1,\cdots n}$ to a basis of B, which is $\{|\phi_j\rangle_B\}_{j=1,\cdots N}$. Now we compute $\hat{\rho}_A$ and $\hat{\rho}_B$,

$$\begin{aligned}
\hat{\rho}_A = Tr_B|\Phi\rangle\langle\Phi| &= \sum_{j=1}^N \langle\phi|_B\Phi\rangle\langle\Phi|\phi_j\rangle_B \\
&= \sum_{j=1}^N\sum_{i=1}^n |v_i|^2(\langle\phi_j|\phi_i\rangle\langle\phi_i|\phi_j\rangle)_B(|\psi_i\rangle\langle\psi_i|)_A = \sum_{i=1}^n |v_i|^2(|\psi_i\rangle\langle\psi_i)_A, \qquad (22)\\
\hat{\rho}_B = Tr_A|\Phi\rangle\langle\Phi| &= \sum_{j=1}^n \langle\psi|_A\Phi\rangle\langle\Phi|\psi_j\rangle_A \\
&= \sum_{j=1}^n\sum_{i=1}^n |v_i|^2(\langle\psi_j|\psi_i\rangle\langle\psi_i|\psi_j\rangle)_A(|\phi_i\rangle\langle\phi_i|)_B = \sum_{i=1}^n |v_i|^2(|\phi_i\rangle\langle\phi_i)_B, \qquad (23)\\
& \qquad (24)
\end{aligned}$$

Since the sets $\{|\psi_j\rangle_A\}_{j=1,\cdots n}$ and $\{|\phi_j\rangle_B\}_{j=1,\cdots N}$ are orthonormal, we see that they are eigenvectors of $\hat{\rho}_A$ and $\hat{\rho}_B$, with corresponding eigenvalues $\{|v_1|^2, \cdots, |v_n|^2\}$ and $\{|v_1|^2, \cdots, |v_n|^2, 0, \cdots, 0\}$, respectively.

2. Given this state, we compute the reduced density matrices to be

$$\hat{\rho}_A = \frac{1}{2}\begin{pmatrix} 1 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 1 \end{pmatrix}, \tag{25}$$

$$\hat{\rho}_B = \frac{1}{4}\begin{pmatrix} 1 & 1 \\ 1 & 3 \end{pmatrix}, \tag{26}$$

$\hat{\rho}_A$ has eigenvalues $\lambda_\pm = \frac{1}{4}(2 \pm \sqrt{2})$, with corresponding eigenvectors $|\pm\rangle_A = \frac{1}{\sqrt{2}}(|\uparrow\rangle \pm |\downarrow\rangle)$. $\hat{\rho}_B$ also has eigenvalues $\lambda_\pm = \frac{1}{4}(2 \pm \sqrt{2})$, with corresponding eigenvectors $|\pm\rangle_B = \frac{1}{\sqrt{4\mp 2\sqrt{2}}}((-1 \pm \sqrt{2})|\uparrow\rangle + |\downarrow\rangle)$.

Therefore

$$|\Phi\rangle = \sum_{\alpha=\pm} \sqrt{\lambda_\alpha}|\alpha\rangle_A \otimes |\alpha_B\rangle \tag{27}$$

Problem 3 Stark effect

Consider a hydrogen atom in the ground state $n = 1$ in a homogeneous electric field $\mathbf{E} = E\hat{e}_z$. The field can be considered as a perturbation. The Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{28}$$

where $\hat{H}_0$ represents the unperturbed hydrogen atom and $\hat{V} = -eE\hat{z}$ corresponds to the perturbation term. Calculate the energy correction of the ground state in leading order.

1. Show that the energy correction vanishes to first order $E_1^{(1)} = 0$. Use the parity operator $\hat{P}$ for this. (Hint: The eigenstates of the hydrogen atom transform as $\hat{P}|nlm\rangle = (-1)^l|nlm\rangle$ and $\hat{P}\hat{z}\hat{P}^\dagger = -\hat{z}$. In addition, $\hat{P}^\dagger\hat{P} = \hat{1}$.)
2. Show that the matrix elements $\langle 100|\hat{z}|nml\rangle$ are finite only for $l = 1$ and $m = 0$. (Hint: z can be expressed using spherical harmonics. Also use their orthogonality.)
3. Calculate the second order energy correction $E_1^{(2)}$ where only states with $n = 2$ need to be considered. States with higher excitation energies $n \geq 3$ can be neglected.

Solution 3

1. The energy correction in first order is

$$E_1^{(1)} = \langle 100|\hat{V}|100\rangle = -eE\langle 100|\hat{z}|100\rangle \tag{29}$$

The fact that the matrix element disappears can be shown by considering the parity

$$\langle 100|\hat{z}|100\rangle = \langle 100|\hat{P}^\dagger\hat{P}\hat{z}\hat{P}^\dagger\hat{P}|100\rangle = -\langle 100|\hat{z}|100\rangle \tag{30}$$

which can only be satisfied by $\langle 100|\hat{z}|100\rangle = 0$.

2. The selection rules for calculating matrix elements for eigenstates of angular momentum operators can only be derived via more complex considerations, such as the Wigner-Eckart theorem. Therefore, the explicit integral must (unfortunately) be considered here.

When calculating the matrix elements, it is used that z can be represented by spherical surface functions $Y_{l,m}(\theta,\phi)$

$$z = r\cos\theta = \sqrt{\frac{4\pi}{3}}rY_{1,0}(\theta,\phi) = \sqrt{\frac{4\pi}{3}}rY_{1,0}^*(\theta,\phi) \tag{31}$$

Thus, with $\langle r\theta\phi|nml\rangle = u_{n,l}(r)Y_{l,m}(\theta,\phi)$, and $\langle r\theta\phi|100\rangle = \frac{1}{\sqrt{4\pi}}u_{1,0}(r)$ the matrix elements become

$$\langle 100|\hat{z}|nml\rangle = \int_0^\infty r^2dr\int_0^\pi \sin\theta d\theta\int_0^{2\pi} d\phi\frac{u_{1,0}^*(r)}{\sqrt{4\pi}}\sqrt{\frac{4\pi}{3}}rY_{1,0}^*(\theta,\phi)Y_{l,m}(\theta,\phi)u_{n,l}(r). \tag{32}$$

If we consider the purely angle-dependent part, we find, using the orthogonality of the spherical harmonics,

$$\langle 100|\hat{z}|nml\rangle \sim \int_0^\pi \sin\theta d\theta\int_0^{2\pi} d\phi Y_{1,0}^*(\theta,\phi)Y_{l,m}(\theta,\phi) \sim \delta_{1,l}\delta_{0,m} \tag{33}$$

from which $l = 1$ and $m = 0$ follows.

3. The second order energy correction is

$$E_1^{(2)} = e^2 E^2 \sum_{nml} \frac{|\langle 100|\hat{z}|nlm\rangle|^2}{E_1 - E_n} \approx e^2 E^2 \frac{|\langle 100|\hat{z}|210\rangle|^2}{E_1 - E_2} \tag{34}$$

where we restrict ourselves to states with $n = 2$. The matrix element is

$$\begin{aligned}\langle 100|\hat{z}|210\rangle &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \frac{u_{1,0}^*(r)}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} r Y_{1,0}^*(\theta,\phi) Y_{1,0}(\theta,\phi) u_{2,1}(r) \\ &= \int_0^\infty dr r^2 \frac{2e^{-r/a_0}}{\sqrt{4\pi} a_0^{3/2}} \sqrt{\frac{4\pi}{3}} r \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/(2a_0)} \\ &= \frac{2^8}{3^5} \frac{a_0}{\sqrt{2}} \end{aligned} \tag{35}$$

where it was used that $\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y_{1,0}^*(\theta,\phi) Y_{1,0}(\theta,\phi) = 1$ and

$$u_{1,0}(r) = \frac{2e^{-r/a_0}}{a_0^{3/2}}, \tag{36}$$

$$u_{2,1}(r) = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/(2a_0)} \tag{37}$$

Thus,

$$E_1^{(2)} = e^2 E^2 \frac{2^{15}}{3^{10}} \frac{a_0^2}{E_1 - E_2} = -e^2 E^2 \frac{2^{15}}{3^{10}} \frac{4}{3R_0} a_0^2 = -\frac{2^{18}}{3^{11}} a_0^3 E^2 \tag{38}$$

with Rydberg Energy $R_0 = \frac{\hbar^2}{2ma_0^2} = \frac{e^2}{2a_0}$.