Problem Set #4, Due: Wednesday February 15 by 11:00am

PHY 362K - Quantum Mechanics II, UT Austin, Spring 2017
(Dated: February 15, 2017)

I. PERTURBED HARMONIC OSCILLATOR

Consider a perturbed Harmonic oscillator with Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{1}$$

where the "bare" Hamiltonian is:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{2}$$

and we perturb with a linear potential:

$$\hat{V} = g\hat{x} \tag{3}$$

where g is a constant.

1. Perturbatively compute the energy levels of $\hat{H}$ to second order in V and the energy eigenstates to first order in V.

   Solution: The first order correction to the energy levels is given by

   $$E_n^1 = \langle n^0|\hat{V}|n^0\rangle = g\langle n^0|\hat{x}|n^0\rangle$$

   We can write $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)$, making this substitution and recalling that $\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$, we find:

   $$\begin{aligned} E_n^1 &= g\sqrt{\frac{\hbar}{2m\omega}}\left(\langle n^0|\hat{a}|n^0\rangle + \langle n^0|\hat{a}^\dagger|n^0\rangle\right) \\ &= g\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\langle n^0|(n-1)^0\rangle + \sqrt{n+1}\langle n^0|(n-1)^0\rangle\right) \end{aligned}$$

   but the states $|n^0\rangle$ are orthogonal, so this expression reduces to

   $$\boxed{E_n^1 = 0} \tag{4}$$

   The second order correction to the energy levels is given by

   $$E_n^2 = \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{|\langle m^0|\hat{V}|n^0\rangle|^2}{E_n^0 - E_m^0} = g^2 \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{|\langle m^0|\hat{x}|n^0\rangle|^2}{E_n^0 - E_m^0}$$

   writing $\hat{x}$ in terms of the creation and annihilation operators, this becomes

   $$E_n^2 = g^2\frac{\hbar}{2m\omega} \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{|\langle m^0|\hat{a} + \hat{a}^\dagger|n^0\rangle|^2}{E_n^0 - E_m^0}$$

but we know that the ground state energies of the unperturbed harmonic oscillator are $E_n^0 = \hbar\omega(n + 1/2)$, so we can write

$$\begin{aligned}
E_n^2 &= g^2 \frac{\hbar}{2m\omega} \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{|\langle m^0|\hat{a}|n^0\rangle + \langle m^0|\hat{a}^\dagger|n^0\rangle|^2}{\hbar\omega(n+1/2) - \hbar\omega(m+1/2)} \\
&= \frac{g^2}{2m\omega^2} \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{|\sqrt{n}\langle m^0|(n-1)^0\rangle + \sqrt{n+1}\langle m^0|(n+1)^0\rangle|^2}{n-m} \\
&= \frac{g^2}{2m\omega^2} \left(\frac{|\sqrt{n}|^2}{n-(n-1)} + \frac{|\sqrt{n+1}|^2}{n-(n+1)} \right)
\end{aligned}$$

where the last line follows from the orthogonality of the energy eigenstates of the unperturbed Hamiltonian, $|n^0\rangle$. Simplifying, we find

$$\boxed{E_n^2 = -\frac{g^2}{2m\omega^2}} \tag{5}$$

The first order correction to the energy eigenstates is given by

$$\begin{aligned}
|n^1\rangle &= \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{\langle m^0|\hat{V}|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle = g\sqrt{\frac{\hbar}{2m\omega}} \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{\langle m^0|\hat{a}+\hat{a}^\dagger|n^0\rangle}{\hbar\omega(n+1/2) - \hbar\omega(m+1/2)}|m^0\rangle \\
&= \frac{g}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}} \sum_{\substack{m=0 \\ m\neq n}}^{\infty} \frac{\sqrt{n}\langle m^0|(n-1)^0\rangle + \sqrt{n+1}\langle m^0|(n+1)^0\rangle}{n-m}|m^0\rangle \\
&= \frac{g}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}} \left[\frac{\sqrt{n}}{n-(n-1)}|(n-1)^0\rangle + \frac{\sqrt{n+1}}{n-(n+1)}|(n+1)^0\rangle \right]
\end{aligned}$$

where the last line follows from the orthogonality of the energy eigenstates of the unperturbed Hamiltonian. Simplifying, we find

$$\boxed{|n^1\rangle = \frac{g}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}} \left[\sqrt{n}|(n-1)^0\rangle - \sqrt{n+1}|(n+1)^0\rangle\right]} \tag{6}$$

2. What is the condition on g for this perturbative approximation to be accurate?

   Solution: The energy scale of the problem is given by $\hbar\omega$, and the length scale of the problem is given by the coefficient of the creation and annihilation operators in the expression for $\hat{x}$, $\sqrt{\frac{\hbar}{2m\omega}}$. Now, g has units of energy per length, and the energy per length scale of the problem is given by $\frac{\hbar\omega}{\sqrt{\frac{\hbar}{2m\omega}}} = \sqrt{2m\hbar\omega^3}$. Therefore, we can say that the perturbative approximation is accurate as long as

   $$\frac{|g|}{\sqrt{2m\hbar\omega^3}} \ll 1$$

3. Why does the first order correction to energy vanish? (Hint: consider the symmetries of the $\frac{1}{2}m\omega^2\hat{x}^2$ potential). Similarly, can you explain the presence/absence of even/odd n terms in the first order correction to the energy eigenstates?

Solution: Let $\hat{P}$ be the parity operator, which is a unitary operator that maps $\hat{x}$ to $-\hat{x}$ and $\hat{p}$ to $-\hat{p}$. Note that since all occurrences of $\hat{x}$ and $\hat{p}$ in $\hat{H}_0$ are raised to an even power, $\hat{H}_0$ is unaffected by the parity operator, which is to say that $\hat{P}^\dagger \hat{H}_0 \hat{P} = \hat{H}_0$. However, since $\hat{V} = g\hat{x}$, $\hat{V}$ switches signs under the parity operator, which is to say that $\hat{P}^\dagger V \hat{P} = -\hat{V}$. Now, note that since $\hat{P}$ is unitary,

$$\hat{P}^\dagger \hat{H}_0 \hat{P} = \hat{H}_0 \implies \hat{H}_0 \hat{P} = \hat{P} \hat{H}_0$$

which is to say that $\hat{H}_0$ and $\hat{P}$ commute. Therefore $\hat{H}_0$ and $\hat{P}$ have simultaneous eigenstates. Therefore $\hat{P}|n^0\rangle = \lambda |n^0\rangle \implies |n^0\rangle = \frac{\hat{P}|n^0\rangle}{\lambda}$. So we can write

$$E_n^1 = \langle n^0 | \hat{V} | n^0 \rangle = \frac{\langle n^0 | \hat{P}^\dagger \hat{V} \hat{P} | n^0 \rangle}{\lambda^* \lambda} = \frac{\langle n^0 | (-\hat{V}) | n^0 \rangle}{\lambda^* \lambda}$$

but $\hat{P}$ is unitary, so $|\lambda|^2 = 1$, therefore

$$E_n^1 = -\langle n^0 | \hat{V} | n^0 \rangle = -E_n^1 \implies E_n^1 = 0$$

So the fact that H_0 is symmetric under parity while the perturbation $\hat{V}$ is antisymmetric forces the first order correction to the energy to vanish.

For odd n, the $|n^1\rangle$ correction is a superposition of only even $|m^0\rangle$ states, while for even n, the $|n^1\rangle$ correction is a superposition of only even $|m^0\rangle$ states. This is because the perturbation is proportional to $\hat{x}$, which is in turn proportional to $\hat{a}^\dagger + \hat{a}$. This sum of creation and annihilation operators has the effect of transforming a state $|n^0\rangle$ to a sum of states $|(n-1)^0\rangle$ and $|(n+1)^0\rangle$. It follows that if n is even (odd) this is a sum of two odd (even) n terms.

4. This problem can also be exactly solved (without much effort – try changing variables to re-write it as a different harmonic oscillator Hamiltonian). What are the exact energies? How does this compare to the perturbative approximation for small g? (Hint: you might also use this to check your answer to the previous parts.)

Solution: By completing the square, we can write

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 + g\hat{x} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \left(\hat{x} + \frac{g}{m\omega^2} \right)^2 - \frac{g^2}{2m\omega^2}$$

if we then make the change of variables $\hat{y} = \hat{x} + \frac{g}{m\omega^2}$, the Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{y}^2 - \frac{g^2}{2m\omega^2}$$

Applying $\hat{H}$ to an eigenstate, $|n\rangle$ of the harmonic oscillator Hamiltonian $\frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{y}^2$, we find

$$\hat{H}|n\rangle = \left(\frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{y}^2 \right) |n\rangle - \frac{g^2}{2m\omega^2} |n\rangle = \left(\hbar\omega(n + 1/2) - \frac{g^2}{2m\omega^2} \right) |n\rangle$$

so the exact energies are

$$\boxed{E_n = \hbar\omega(n + 1/2) - \frac{g^2}{2m\omega^2}} \tag{7}$$

This agrees exactly with our perturbative approximation.

II. HIGHER ORDERS IN PERTURBATION THEORY AND WAVE-FUNCTION RENORMALIZATION

Consider a generic Hamiltonian:

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \tag{8}$$

As in class, we will treat $\lambda\hat{V}$ as a perturbation and expand the full eigenstates, $|n\rangle$, and eigenenergies, ε_n of $\hat{H}$ in a power series in λ:

$$\begin{aligned}|n\rangle &= \sqrt{Z_n}\left(\sum_{k=0}^{\infty}\lambda^k|n^k\rangle\right)\\ \varepsilon_n &= \sum_{k=0}^{\infty}\lambda^k\varepsilon_n^k\end{aligned} \tag{9}$$

where $|n^0\rangle$ are the eigenstates of the unperturbed Hamiltonian, $\hat{H}_0$: $\hat{H}_0|n^0\rangle = \varepsilon_n^0|n^0\rangle$You may assume that: $\varepsilon_n^0 \neq \varepsilon_m^0$ for all $m \neq n$ (i.e. there are no degeneracies).

In class we worked out expressions for $|n^1\rangle$ and $\varepsilon_n^{1,2}$.

1. Wave-function (re)normalization: The normalization constant Z_n dropped out of the eigenvalue equation for $\hat{H}$. However, properly normalizing $|n\rangle$ becomes important if we want to compute, say, the expectation value $\langle n|\hat{O}|n\rangle$ of other observables, $\hat{O}$. Note that since $Z_n = |\langle n_0|n\rangle|^2$, we can physically interpret this quantity as the probability that a particle in the exact $\hat{H}$-eigenstate $|n\rangle$ is measured in the the unperturbed eigenstate $|n^0\rangle$.

   (a) Find Z_n up to second order in λ so that $|n\rangle$ is properly normalized ($\langle n|n\rangle = 1$). At what order in λ does the first non-zero correction to $Z_n^0 = 1$ appear?

   Solution: For $|n\rangle$ to be properly normalized, we must have $\langle n|n\rangle = 1$. Substituting the power series expression for $|n\rangle$, we find:

$$\begin{aligned}\langle n|n\rangle &= 1\\ \left(\sqrt{Z_n}\sum_{m=0}^{\infty}\lambda^m\langle n^m|\right)\left(\sqrt{Z_n}\sum_{k=0}^{\infty}\lambda^k|n^k\rangle\right) &= 1\\ Z_n\sum_{m,k=0}^{\infty}\lambda^{m+k}\langle n^m|n^k\rangle &= 1\end{aligned}$$

   expanding to second order in λ, we find

$$\langle n|n\rangle = Z_n\left(\langle n^0|n^0\rangle + \lambda(\langle n^0|n^1\rangle + \langle n^1|n^0\rangle) + \lambda^2(\langle n^1|n^1\rangle + \langle n^2|n^0\rangle + \langle n^0|n^2\rangle)\right) = 1$$

   Since we can write $|n^1\rangle$ and $|n^2\rangle$ as linear combinations of $|m^0\rangle, m \neq n$, it follows from the orthogonality of the unperturbed eigenstates that $\langle n^1|n^0\rangle = \langle n^0|n^1\rangle = \langle n^2|n^0\rangle = \langle n^0|n^2\rangle = 0$. Therefore,

$$\langle n|n\rangle = Z_n\left(1 + \lambda^2\langle n^1|n^1\rangle\right) = 1$$

Substituting the expression for $|n^1\rangle$ in terms of the unperturbed eigenstates, $|n^1\rangle = \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{\langle m^0|\hat{V}|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle$, we find

$$Z_n \left(1 + \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \sum_{\substack{k=0\\k\neq n}}^{\infty} \frac{\langle n^0|\hat{V}|m^0\rangle}{E_n^0 - E_m^0} \frac{\langle k^0|\hat{V}|n^0\rangle}{E_n^0 - E_k^0} \langle m^0|k^0\rangle \right) = 1$$

$$Z_n \left(1 + \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{(E_n^0 - E_m^0)^2} \right) = 1$$

where the last line follows from the orthonormality of the unperturbed eigenstates. Therefore,

$$Z_n = \left(1 + \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{(E_n^0 - E_m^0)^2} \right)^{-1}$$

If we now perform a binomial expansion to second order in lambda, we find

$$\boxed{Z_n = 1 - \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{(E_n^0 - E_m^0)^2}} \tag{10}$$

The first non-zero correction to $Z_n = 1$ occurs at second order in λ.

(b) Show, to this order, that $Z_n = \dfrac{\partial \varepsilon_n}{\partial \varepsilon_n^0}$ (Note: though you will demonstrate this up to second order in λ, this relationship actually holds to all orders!).

Solution: We know that we can write $E_n = \sum_{k=0}^{\infty} \lambda^k E_n^k$, expanding this to second order in λ, we have $E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2$. But $E_n^1 = \langle n^0|\hat{V}|n^0\rangle$ and $E_n^2 = \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{E_n^0 - E_m^0}$, so we can write

$$E_n = E_n^0 + \lambda\langle n^0|\hat{V}|n^0\rangle + \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{E_n^0 - E_m^0}$$

Differentiating with respect to E_n^0, we obtain

$$\frac{\partial E_n}{\partial E_n^0} = 1 - \lambda^2 \sum_{\substack{m=0\\m\neq n}}^{\infty} \frac{|\langle n^0|\hat{V}|m^0\rangle|^2}{(E_n^0 - E_m^0)^2}$$

However, to second order in λ, this equals the expression we obtained for Z_n in part (a), therefore $Z_n = \frac{\partial E_n}{\partial E_n^0}$.

2. Next Higher order terms: Compute the expression for the second order correction to the energy eigenstates, $|n^2\rangle$, and third order correction to the energies, ε_n^3 in terms of the unperturbed eigenstates and energies of $\hat{H}_0$.

   Solution: Substituting the power series expansion of $|n\rangle$ and E_n into the time independent Schrodinger equation, $\hat{H}|n\rangle = E_n|n\rangle$ produces

$$(\hat{H}_0 + \lambda\hat{V})\sum_{k=0}^{\infty}\lambda^k|n^k\rangle = \left(\sum_{m=0}^{\infty}\lambda^m E_n^m\right)\left(\sum_{k=0}^{\infty}\lambda^k|n^m\rangle\right)$$

   collecting like powers of λ and equating, we find that the coefficients of λ^2 produce the equation

$$\hat{H}_0|n^2\rangle + \hat{V}|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle \tag{11}$$

   and the coefficients of λ^3 produce the equation

$$\hat{H}_0|n^3\rangle + \hat{V}|n^2\rangle = E_n^0|n^3\rangle + E_n^1|n^2\rangle E_n^2|n^1\rangle + E_n^3|n^0\rangle \tag{12}$$

   We will begin by finding the second order correction to the energy eigenstates, $|n^2\rangle$. If we take the inner product of both sides of equation 11 with $|m^0\rangle$, where $m \neq n$, then we find

$$\langle m^0|\hat{H}_0|n^2\rangle + \langle m^0|\hat{V}|n^1\rangle = E_n^0\langle m^0|n^2\rangle + E_n^1\langle m^0|n^1\rangle + E_n^2\langle m^0|n^0\rangle$$

   rearranging and using the hermiticity of $\hat{H}_0$ to write $\langle m_0|\hat{H}_0|n^2\rangle = E_m^0\langle m^0|n^2\rangle$, we have

$$(E_m^0 - E_n^0)\langle m^0|n^2\rangle = E_n^1\langle m^0|n^1\rangle - \langle m^0|\hat{V}|n^1\rangle$$
$$\langle m^0|n^2\rangle = \frac{E_n^1\langle m^0|n^1\rangle - \langle m^0|\hat{V}|n^1\rangle}{E_m^0 - E_n^0}$$

   We can write $|n^2\rangle = \sum_{\substack{m=0\\m\neq n}}^{\infty}\langle m^0|n^2\rangle|m^0\rangle$, therefore the second order correction to the energy eigenstates is

$$\boxed{|n^2\rangle = \sum_{\substack{m=0\\m\neq n}}^{\infty}\frac{E_n^1\langle m^0|n^1\rangle - \langle m^0|\hat{V}|n^1\rangle}{E_m^0 - E_n^0}|m^0\rangle} \tag{13}$$

   Now, to find the third order correction to the energies, E_n^3, we will take the inner product of both sides of equation 12 with $|n^0\rangle$. This produces

$$\langle n^0|\hat{H}_0|n^3\rangle + \langle n^0|\hat{V}|n^2\rangle = E_n^0\langle n^0|n^2\rangle + E_n^1\langle n^0|n^2\langle + E_n^2\langle n^0|n^1\rangle + E_n^3\langle n^0|n^0\rangle$$

   rearranging and using the hermiticity of $\hat{H}_0$ to write $\langle n^0|\hat{H}_0|n^3\rangle = E_n^0\langle n^0|n^3\rangle$, we obtain

$$E_n^3 = \langle n^0|\hat{V}|n^2\rangle - E_n^1\langle n^0|n^2\rangle - E_n^2\langle n^0|n^1\rangle$$

   However, we can write $|n^1\rangle$ and $|n^2\rangle$ as a linear combination of $|m^0\rangle$, with $m \neq n$, therefore $\langle n^0|n^1\rangle = \langle n^0|n^2 \;= 0$, so the expression simplifies to

$$E_n^3 = \langle n^0|\hat{V}|n^2\rangle$$

   substituting the expression for $|n^2\rangle$ that we found in the last problem, we obtain

$$\boxed{E_n^3 = \sum_{\substack{m=0\\m\neq n}}^{\infty}\frac{E_n^1\langle m^0|n^1\rangle - \langle m^0|\hat{V}|n^1\rangle}{E_m^0 - E_n^0}\langle n^0|\hat{V}|m^0\rangle} \tag{14}$$

III. DEGENERATE PERTURBATION THEORY EXAMPLE – TWO SPINS-1/2

Consider two spins-1/2, with spin-operators $\hat{\mathbf{S}}_{1,2} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$, where $\sigma^{x,y,z}$ are Pauli operators, and Hamiltonian:

$$H = J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + g\hat{S}_1^x\left(\frac{1}{\hbar}\hat{S}_2^z + \frac{1}{2}\right) \tag{15}$$

Suppose that, $J, g > 0$, and $g \ll J$, and compute the energy-eigenstates to first order in g, and the energies to second order in g (be sure to properly take care of any degeneracies).

Hint: to solve for the unperturbed eigenstates with $g = 0$, you can use that $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2}\left[\left(\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2\right)^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2\right]$, and the properties of adding angular momentum that you learned last semester.

Solution: First, we will find the eigenstates of the unperturbed Hamiltonian, $\hat{H}_0 = J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = J(S_1^x S_2^x + S_1^y S_2^y + S_1^z S_2^z)$. By direct calculation, we find

$$J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2|\uparrow\uparrow\rangle = J\frac{\hbar^2}{4}(|\downarrow\downarrow\rangle + i^2|\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle) = J\frac{\hbar^2}{4}|\uparrow\uparrow\rangle$$
$$J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2|\downarrow\downarrow\rangle = J\frac{\hbar^2}{4}(|\uparrow\uparrow\rangle + i^2|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) = J\frac{\hbar^2}{4}|\downarrow\downarrow\rangle$$
$$J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2\left[\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)\right] = J\frac{\hbar^2}{4\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle - i^2|\downarrow\uparrow\rangle - i^2|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = J\frac{\hbar^2}{4\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$
$$J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2\left[\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\right] = J\frac{\hbar^2}{4\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle - i^2|\downarrow\uparrow\rangle + i^2|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = J\frac{3\hbar^2}{4\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

Therefore, the eigenvectors of the unperturbed Hamiltonian are $|1^0\rangle = |\uparrow\uparrow\rangle$ with eigenvalue $E_1^0 = J\frac{\hbar^2}{4}$, $|2^0\rangle = |\downarrow\downarrow\rangle$ with eigenvalue $E_2^0 = J\frac{\hbar^2}{4}$, $|3^0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ with eigenvalue $E_3^0 = J\frac{\hbar^2}{4}$, and $|4^0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ with eigenvalue $E_4^0 = -J\frac{3\hbar^2}{4}$.

Note that there are three degenerate states that share the energy $J\frac{\hbar^2}{4}$. We will now construct the matrix that represents the perturbation, $\hat{V} = g\hat{S}_1^x\left(\frac{1}{\hbar}\hat{S}_2^z + \frac{1}{2}\right)$, in the subspace spanned by these degenerate states. We begin by computing

$$\hat{V}|1^0\rangle = g\hat{S}_1^x\left(\frac{1}{\hbar}\hat{S}_2^z + \frac{1}{2}\right)|\uparrow\uparrow\rangle = \frac{g\hbar}{2}|\downarrow\uparrow\rangle$$
$$\hat{V}|2^0\rangle = g\hat{S}_1^x\left(\frac{1}{\hbar}\hat{S}_2^z + \frac{1}{2}\right)|\downarrow\downarrow\rangle = 0$$
$$\hat{V}|3^0\rangle = g\hat{S}_1^x\left(\frac{1}{\hbar}\hat{S}_2^z + \frac{1}{2}\right)\left[\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)\right] = \frac{g\hbar}{2\sqrt{2}}|\uparrow\uparrow\rangle$$

we can now find the matrix form of $\hat{V}$:

$$\begin{pmatrix} \langle 1^0|\hat{V}|1^0\rangle & \langle 1^0|\hat{V}|2^0\rangle & \langle 1^0|\hat{V}|3^0\rangle \\ \langle 2^0|\hat{V}|1^0\rangle & \langle 2^0|\hat{V}|2^0\rangle & \langle 3^0|\hat{V}|2^0\rangle \\ \langle 3^0|\hat{V}|1^0\rangle & \langle 3^0|\hat{V}|2^0\rangle & \langle 3^0|\hat{V}|3^0\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 & \frac{g\hbar}{2\sqrt{2}} \\ 0 & 0 & 0 \\ \frac{g\hbar}{2\sqrt{2}} & 0 & 0 \end{pmatrix}$$

By inspection, we can see that the eigenvalues of this matrix are $|1^{0\prime}\rangle = \frac{1}{\sqrt{2}}(|1^0\rangle + |3^0\rangle)$ with eigenvalue $\frac{g\hbar}{2\sqrt{2}}$, $|2^0\rangle$ with eigenvalue 0, and $|3^{0\prime}\rangle = \frac{1}{\sqrt{2}}(|1^0\rangle - |3^0\rangle)$ with eigenvalue $-\frac{g\hbar}{2\sqrt{2}}$. So in the new basis $\{|1^{0\prime}\rangle, |2^0\rangle, |3^{0\prime}\rangle, |4^0\rangle\}$, the matrix representing $\hat{V}$ is diagonal and we can use the results of non-degenerate perturbation theory.

Now the first order energy corrections are

$$
\begin{aligned}
E_1^1 &= \langle 1^{0\prime}|\hat{V}|1^{0\prime}\rangle = \frac{g\hbar}{2\sqrt{2}} \\
E_2^1 &= \langle 2^0|\hat{V}|2^0\rangle = 0 \\
E_3^1 &= \langle 3^{0\prime}|\hat{V}|3^{0\prime}\rangle = -\frac{g\hbar}{2\sqrt{2}} \\
E_4^1 &= \langle 4^0|\hat{V}|4^0\rangle = -\frac{g\hbar}{4\sqrt{2}}(\langle\uparrow\downarrow| - \langle\uparrow\downarrow|)|\uparrow\uparrow\rangle = 0
\end{aligned}
$$

The second order energy corrections are

$$
\begin{aligned}
E_1^2 &= \frac{|\langle 2^0|\hat{V}|1^{0\prime}\rangle|^2}{E_1^0 - E_2^0} + \frac{|\langle 3^{0\prime}|\hat{V}|1^{0\prime}\rangle|^2}{E_1^0 - E_3^0} + \frac{|\langle 4^0|\hat{V}|1^{0\prime}\rangle|^2}{E_1^0 - E_4^0} \\
&= \frac{|\langle 4^0|\hat{V}|1^{0\prime}\rangle|^2}{E_1^0 - E_4^0} = \frac{\left|\frac{g\hbar}{4}(\langle\downarrow\uparrow| - \langle\uparrow\downarrow|)(|\downarrow\uparrow\rangle + \frac{1}{\sqrt{2}}|\uparrow\uparrow\rangle)\right|^2}{J\hbar^2(\frac{1}{4} + \frac{3}{4})} \\
&= \frac{\left|\frac{g\hbar}{4}\right|^2}{J\hbar^2} = \frac{g^2}{16J} \\
E_2^2 &= \frac{|\langle 1^{0\prime}|\hat{V}|2^0\rangle|^2}{E_2^0 - E_1^0} + \frac{|\langle 3^{0\prime}|\hat{V}|2^0\rangle|^2}{E_2^0 - E_3^0} + \frac{|\langle 4^0|\hat{V}|2^0\rangle|^2}{E_2^0 - E_4^0} \\
&= \frac{|\langle 4^0|\hat{V}|2^0\rangle|^2}{E_2^0 - E_4^0} = \frac{|0|^2}{E_2^0 - E_4^0} = 0 \\
E_3^2 &= \frac{|\langle 1^{0\prime}|\hat{V}|3^{0\prime}\rangle|^2}{E_3^0 - E_1^0} + \frac{|\langle 2^0|\hat{V}|3^{0\prime}\rangle|^2}{E_3^0 - E_2^0} + \frac{|\langle 4^0|\hat{V}|3^{0\prime}\rangle|^2}{E_3^0 - E_4^0} \\
&= \frac{|\langle 4^0|\hat{V}|3^{0\prime}\rangle|^2}{E_3^0 - E_4^0} = \frac{\left|\frac{g\hbar}{2\sqrt{2}}(\langle\downarrow\uparrow| - \langle\uparrow\downarrow|)|\uparrow\uparrow\rangle\right|^2}{J\hbar^2(\frac{1}{4} + \frac{3}{4})} = 0 \\
E_4^2 &= \frac{|\langle 1^{0\prime}|\hat{V}|4^0\rangle|^2}{E_4^0 - E_1^0} + \frac{|\langle 2^0|\hat{V}|4^0\rangle|^2}{E_4^0 - E_2^0} + \frac{|\langle 3^{0\prime}|\hat{V}|4^0\rangle|^2}{E_4^0 - E_3^0} \\
&= -\frac{1}{J\hbar^2}\left|-\frac{g\hbar}{2\sqrt{2}}\right|^2 \left(|\langle 1^{0\prime}|\downarrow\downarrow\rangle|^2 + |\langle 2^0|\downarrow\downarrow\rangle|^2 + |\langle 3^{0\prime}|\downarrow\downarrow\rangle|^2\right) = -\frac{g^2}{8J}
\end{aligned}
$$

The first order eigenstate corrections are:

$$
\begin{aligned}
|1^1\rangle &= \frac{\langle 2^0|\hat{V}|1^{0\prime}\rangle}{E_1^0 - E_2^0}|2^0\rangle + \frac{\langle 3^{0\prime}|\hat{V}|1^{0\prime}\rangle}{E_1^0 - E_3^0}|3^0\rangle + \frac{\langle 4^0|\hat{V}|1^{0\prime}\rangle}{E_1^0 - E_4^0}|4^0\rangle \\
&= \frac{\langle 4^0|\hat{V}|1^{0\prime}\rangle}{E_1^0 - E_4^0}|4^0\rangle = -\frac{g}{4J\hbar}|4^0\rangle \\
|2^1\rangle &= \frac{\langle 1^{0\prime}|\hat{V}|2^0\rangle}{E_2^0 - E_1^0}|1^{0\prime}\rangle + \frac{\langle 3^{0\prime}|\hat{V}|2^0\rangle}{E_2^0 - E_3^0}|3^{0\prime}\rangle + \frac{\langle 4^0|\hat{V}|2^0\rangle}{E_2^0 - E_4^0}|4^0\rangle = \frac{\langle 4^0|\hat{V}|2^0\rangle}{E_2^0 - E_4^0}|4^0\rangle \\
&= \frac{0}{E_4^0 - E_2^0}|4^0\rangle = 0 \\
|3^1\rangle &= \frac{\langle 1^{0\prime}|\hat{V}|3^{0\prime}\rangle}{E_3^0 - E_1^0}|1^{0\prime}\rangle + \frac{\langle 2^0|\hat{V}|3^{0\prime}\rangle}{E_3^0 - E_2^0}|3^{0\prime}\rangle + \frac{\langle 4^0|\hat{V}|3^{0\prime}\rangle}{E_3^0 - E_4^0}|4^0\rangle = \frac{\langle 4^0|\hat{V}|3^0\rangle}{E_4^0 - E_3^0}|4^0\rangle \\
&= -\frac{g}{4J\hbar}|4^0\rangle \\
|4^1\rangle &= \frac{\langle 1^{0\prime}|\hat{V}|4^0\rangle}{E_1^0 - E_4^0}|1^{0\prime}\rangle + \frac{\langle 2^0|\hat{V}|4^0\rangle}{E_2^0 - E_4^0}|2^0\rangle + \frac{\langle 3^0|\hat{V}|4^0\rangle}{E_3^0 - E_4^0}|3^0\rangle \\
&= 0 + 0 + \frac{g}{2\sqrt{2}J}|2^0\rangle = \frac{g}{2\sqrt{2}J}|2^0\rangle
\end{aligned}
$$

So to second order in g, the energies are

$$
\begin{aligned}
E_1 &= J\frac{\hbar^2}{4} + \frac{g\hbar}{2\sqrt{2}} + \frac{g^2}{16J} \\
E_2 &= J\frac{\hbar^2}{4} \\
E_3 &= J\frac{\hbar^2}{4} - \frac{g\hbar}{2\sqrt{2}} \\
E_4 &= -J\frac{3\hbar^2}{4} - \frac{g^2}{8J}
\end{aligned} \tag{16}
$$

To first order in g, the eigenstates are:

$$
\begin{aligned}
|1\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle + \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)) - \frac{g}{4J\hbar}\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\
|2\rangle &= |\downarrow\downarrow\rangle \\
|3\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle - \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)) - \frac{g}{4J\hbar}\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\
|4\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) + \frac{g}{2\sqrt{2}J}|\uparrow\uparrow\rangle
\end{aligned} \tag{17}
$$