You may use anything from the 486/7 formula sheets without derivation … but do try to see how far you can get on your own on your Desert Island. ☺

You may also use wolframalpha.com or similar tool to evaluate your integrals after you set the up in a form that can be directly entered into such tools.

Here are the perturbation theory (non-degenerate, time-independent) results we introduced in discussion 5 and will prove in lecture. If you have

- a “zeroth-order” Hamiltonian $H_0$ that has exact eigenvalues $\{E_n^{(0)}\}$ and eigenstates $\{|n^{(0)}\rangle\}$,

- an actual Hamiltonian $H = H_0 + H'$ where $H'$ is a small correction to $H_0$ (a “perturbation”, $H' \ll H_0$),

- a series expansion of $H$ eigenvalues: $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + ...$ for each $n$ where $E_n^{(0)} \gg E_n^{(1)} \gg E_n^{(2)} \gg ...$

- & a series expansion of $H$ eigenstates: $|n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + ...$ for each $n$, where $|n^{(0)}\rangle \gg |n^{(1)}\rangle \gg ...$

then as long as

- the exact eigenstates $\{|n^{(0)}\rangle\}$ are non-degenerate and

- the Hamiltonian $H = H_0 + H'$ has no explicit time-dependence,

then 1\textsuperscript{st}-order and 2\textsuperscript{nd}-order corrections to each unperturbed energy $E_n /$ unperturbed eigenstate $|n^{(0)}\rangle$ are:

$$E_n^{(1)} = \langle n^{(0)}\rangle H' |n^{(0)}\rangle$$

is the expectation value of the perturbation $H'$ in the $n^\text{th}$ exact state.

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

$$|n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m^{(0)}\rangle |H'| n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle$$

For a set of degenerate states, you have to do a bit more work to get the first-order energy correction → see the intro to Discussion 7.

**Problem 1 : The Van der Walls Force — Important for Chemistry!**

*Griffiths 6.31*

Hint for part (d): Remember that the eigenstates of energy of the 1D SHO (as tabulated in Disc06-SHO-reference.pdf for your convenience) are all orthonormal. The integral(s) you have to do can be performed using this fact: The $n^\text{th}$ Hermite polynomial, $H_n(x)$, is a polynomial of order $n$. If you multiply it by $x$, you turn it into a polynomial of order $n+1$ … which you can write as a linear combination of $H_{n+1}(x)$ and $H_{n-1}(x)$. :-)

**Problem 2 : Good Quantum Numbers & Commuting-with-the-Hamiltonian** adapted from Griffiths 6.16

Remember this relation from 436?

$$\frac{d\langle \hat{Q}\rangle}{dt} = \frac{1}{i\hbar} \left[ \hat{Q}, \hat{H} \right] + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle$$

That equation in words: if an observable $\hat{Q}$ has no explicit dependence on time ($\partial Q / \partial t = 0$) and commutes with a system’s Hamiltonian, then its expectation value is a constant of motion. In fact, this is our one and only definition of the phrase “constant of motion” in quantum mechanics.
About that last term: In all the examples below, \( \partial Q/\partial t \), i.e. none of our operators \( Q \) will have any explicit dependence on time. To clarify what that means, we need a counter-example! An example of an observable with an explicit time-dependence would be the potential energy of a spring that is being heated, and thereby becoming weaker with time: \( V(x, t) = \frac{1}{2} k(t) x^2 \) where \( k(t) = k_0 e^{-\nu t} \) or some such thing.

Corollary: If we put a system in an eigenstate \( | q_n > \) of an observable \( Q \), where \( n \) is the quantum number that labels the state’s eigenvalue \( q_n \), then the system will remain in that eigenstate forever as long as the operator associated with \( Q \) commutes with the Hamiltonian of the system and has no explicit time-dependence.

This is one of the most important consequences of commutators!

Important new jargon: A quantum number whose operator commutes with the Hamiltonian is called a good quantum number of the system because it will maintain its value if the system is prepared in an eigenstate.

(a) Prove in one line that \( [AB, C] = A[B, C] + [A, C]B \). You can then use this freely in all subsequent problems.

NOTE: This “calculate \([AB, C]\)” situation is very common: you often know commutators between two observables (e.g. \([x, p]\) or \([L_x, L_y]\)) but need the commutator between products of them (e.g. \([L^2, L_z]\)).

Useful though that formula is, you should certainly not memorize it!! Instead, remember the extremely simple procedure you just used to derive it: subtract a term and add it back!!

(b) Consider the 1D-SHO \(^\text{TM}\) with Hamiltonian

\[
H(x) = \frac{\hbar \omega}{2} \left( \dot{\xi}^2 - \frac{d^2}{d \xi^2} \right) \quad \text{where} \quad \xi \equiv \frac{x}{x_0} \quad \text{and} \quad x_0 \equiv \sqrt{\frac{\hbar}{m \omega}} \quad \text{and} \quad m, \omega \text{ are known constants.}
\]

For convenience, assume we are working in units where \( x_0 = 1 \) (which is always possible!) ☺

(i) Identify 1 or 2 time-independent observables (i.e. Hermitian operators, \( \hat{Q} \), with \( \partial \hat{Q} / \partial t = 0 \) ) that give good quantum numbers for the SHO, and explicitly show that they commute with the Hamiltonian.

Think physically: “I start an SHO = mass+spring in such a way that observable \( Q \) has a definite value; I am looking for a \( Q \) that will keep that same value as time progresses.”

(ii) Identify 1 or 2 time-independent observables that DO NOT give good quantum numbers for the SHO, and explicitly show that they do not commute with the Hamiltonian.

Think physically: “I start an SHO = mass+spring in such a way that observable \( Q \) has a definite value; I am looking for a \( Q \) that will NOT keep that same value as time progresses.”

In TOTAL you must identify at least THREE observables between parts (i) and (ii), but either part may have only one answer.

(c) What observable always produces a good quantum number (as long as it has no explicit \( t \)-dependence)?

(d) Now ask yourself this immense question:

What are the good quantum numbers for atomic electrons?

Hmm! We’ve seen tables of elements where spectroscopic notation \( ^{2S+1} \ell \text{ } \ell_j \) is used to specify the ground state.

To understand why this notation is used, you must calculate 6 commutators:

(i) \([\hat{L} \cdot \hat{S}, \hat{L}]\)  (ii) \([\hat{L} \cdot \hat{S}, \hat{S}]\)  (iii) \([\hat{L} \cdot \hat{S}, \hat{J}]\)  (iv) \([\hat{L} \cdot \hat{S}, \hat{L}^2]\)  (v) \([\hat{L} \cdot \hat{S}, \hat{S}^2]\)  (vi) \([\hat{L} \cdot \hat{S}, J^2]\)

Please do not repeat algebra unnecessarily! Use symmetries / similarities between these various objects to argue things like “since A,B have the same relations as C,D, I can use my result for A,B directly for C,D too”.
