

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

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

$$\boxed{E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle} = \text{the expectation value of the perturbation } H' \text{ in the } n^{\text{th}} \text{ exact state.}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)} | H' | n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad |n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m^{(0)} | H' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle$$

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*

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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?

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

That equation in words: if an **observable  $Q$**  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  $k(t) = k_0 e^{-t/\tau}$  or some such thing.

Corollary: If we **put a system in an eigenstate**  $|q_n\rangle$  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 <sup>TM</sup> with Hamiltonian

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

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**  $^{2S+1}\mathcal{L}_J$  is used to specify the ground state.

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

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

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”.