

## 17 Harmonic oscillator revisited: Dirac's approach and introduction to Second Quantization

1. Dirac came up with a more elegant way to solve the harmonic oscillator problem. We will now study this approach. The reason we want to study this approach is because this, in fact, gives an alternative approach to quantum mechanics and this is known as second quantization. The whole field of quantum field theory is a generalization of the concepts introduced by Dirac in the late 1920s. Second quantization also forms an important portion of modern day research in quantum theory since mathematics generally becomes simpler in second quantization notation.
2. We define a new operator  $a$  as a linear combination of the position and momentum operators:

$$a = \frac{i}{\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} - ik^{1/2} \hat{x} \right) \quad (17.1)$$

This operator is simply a linear combination of the position and momentum operators as we can see. Hence the dual space analogue of this operator is given by:

$$a^\dagger = \frac{1}{i\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} + ik^{1/2} \hat{x} \right) \quad (17.2)$$

Therefore,

$$\begin{aligned}
 a^\dagger a &= \left[ \frac{1}{i\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} + ik^{1/2} \hat{x} \right) \right] \left[ \frac{i}{\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} - ik^{1/2} \hat{x} \right) \right] \\
 &= \frac{1}{\hbar\omega} \left[ \frac{\hat{p}^2}{2m} + \frac{1}{2} k \hat{x}^2 + \frac{i}{2} \left( \frac{k}{m} \right)^{1/2} [\hat{x}, \hat{p}] \right] \quad (17.3)
 \end{aligned}$$

Now,  $[\hat{x}, \hat{p}] = i\hbar$ ,  $\frac{\hat{p}^2}{2m} + \frac{1}{2} k \hat{x}^2 = H$ , the harmonic oscillator Hamiltonian and we defined earlier that  $k = m\omega^2$  as the relation between the force constant and the angular velocity. Therefore,

$$a^\dagger a = \frac{H}{\hbar\omega} - \frac{1}{2} \quad (17.4)$$

Similarly,

$$\begin{aligned}
 aa^\dagger &= \left[ \frac{i}{\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} - ik^{1/2} \hat{x} \right) \right] \left[ \frac{1}{i\sqrt{2\hbar\omega}} \left( \frac{1}{m^{1/2}} \hat{p} + ik^{1/2} \hat{x} \right) \right] \\
 &= \frac{1}{\hbar\omega} \left[ \frac{\hat{p}^2}{2m} + \frac{1}{2} k \hat{x}^2 - \frac{i}{2} \left( \frac{k}{m} \right)^{1/2} [\hat{x}, \hat{p}] \right] \\
 &= \frac{H}{\hbar\omega} + \frac{1}{2} \quad (17.5)
 \end{aligned}$$

Therefore the harmonic oscillator Hamiltonian can be written as

$$H = \frac{1}{2} \hbar\omega [a^\dagger a + aa^\dagger] \quad (17.6)$$

and the commutator

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = 1 \quad (17.7)$$

3. Lets also derive a couple of more commutators  $[a, H]$  and  $[a^\dagger, H]$  that will be useful later.

$$\begin{aligned}[a, H] &= \frac{1}{2}\hbar\omega [aa^\dagger a + a a a^\dagger - a^\dagger a a - a a^\dagger a] \\ &= \frac{1}{2}\hbar\omega [(aa^\dagger - a^\dagger a) a + a (aa^\dagger - a^\dagger a)] \\ &= \hbar\omega a\end{aligned}\tag{17.8}$$

Similarly,

$$\begin{aligned}[a^\dagger, H] &= \frac{1}{2}\hbar\omega [a^\dagger a^\dagger a + a^\dagger a a^\dagger - a^\dagger a a^\dagger - a a^\dagger a^\dagger] \\ &= \frac{1}{2}\hbar\omega [a^\dagger (a^\dagger a - a a^\dagger) + (a^\dagger a - a a^\dagger) a^\dagger] \\ &= -\hbar\omega a^\dagger\end{aligned}\tag{17.9}$$

4. Now, let  $|E\rangle$  be an eigenstate of  $H$  with eigenvalue  $E$ . Therefore,

$$H |E\rangle = E |E\rangle \quad (17.10)$$

Let  $a |E\rangle = |Q\rangle$ , another ket vector. Therefore,

$$\langle E | a^\dagger a | E \rangle = \langle Q | Q \rangle \geq 0 \quad (17.11)$$

This implies

$$\langle E | a^\dagger a | E \rangle = \left\langle E \left| \frac{H}{\hbar\omega} - \frac{1}{2} \right| E \right\rangle = \frac{E}{\hbar\omega} - \frac{1}{2} \geq 0 \quad (17.12)$$

Therefore,  $E \geq \frac{1}{2}\hbar\omega$  !!! This means the energy of the quantum Harmonic oscillator cannot be lower than  $\frac{1}{2}\hbar\omega$ , hence that is the zero-point energy of the oscillator. (Recall that we got the exact same result last time but by solving the differential equation. This time we have done none of that, we have introduced a new algebraic technique, and we have used that to obtain this result in a much easier fashion.) Now it remains to see what the operators  $a$  and  $a^\dagger$  really mean.

5. For this lets consider the following:

$$aH |E\rangle = Ea |E\rangle \quad (17.13)$$

Using the commutation relations:

$$\begin{aligned} (Ha + \hbar\omega a) |E\rangle &= Ea |E\rangle \\ (H + \hbar\omega) [a |E\rangle] &= E [a |E\rangle] \\ H [a |E\rangle] &= (E - \hbar\omega) [a |E\rangle] \end{aligned} \quad (17.14)$$

Therefore the ket vector  $[a |E\rangle]$  is an eigenket of  $H$  with eigenvalue  $(E - \hbar\omega)$ .

6. Similarly consider

$$a^\dagger H |E\rangle = Ea^\dagger |E\rangle \quad (17.15)$$

And using the commutation relations:

$$\begin{aligned} (Ha^\dagger - \hbar\omega a^\dagger) |E\rangle &= Ea^\dagger |E\rangle \\ (H - \hbar\omega) [a^\dagger |E\rangle] &= E [a^\dagger |E\rangle] \\ H [a^\dagger |E\rangle] &= (E + \hbar\omega) [a^\dagger |E\rangle] \end{aligned} \quad (17.16)$$

and the ket vector  $[a^\dagger |E\rangle]$  is an eigenket of  $H$  with eigenvalue  $(E + \hbar\omega)$ .

7. We obtained the relation  $E \geq \frac{1}{2}\hbar\omega$  as a result of Eq. (17.12). This means that the energy can have values only *greater* than (but including)  $\frac{1}{2}\hbar\omega$ . Lets say:

$$H |E_0\rangle = \frac{1}{2}\hbar\omega |E_0\rangle \quad (17.17)$$

where we represent the *ket* vector corresponding to the energy  $\frac{1}{2}\hbar\omega$  by  $|E_0\rangle$ .

8. Now, using Eq. (17.16)

$$H [a^\dagger |E_0\rangle] = \left(\frac{1}{2}\hbar\omega + \hbar\omega\right) [a^\dagger |E_0\rangle] \quad (17.18)$$

since  $\frac{1}{2}\hbar\omega$  is the energy eigenvalue for the ket  $|E_0\rangle$ .

9. Lets now denote the new eigenvector:  $|E_1\rangle = a^\dagger |E_0\rangle$ . Then we can use Eq. (17.16) again on  $|E_1\rangle$  to obtain:

$$H [a^\dagger |E_1\rangle] = \left(\frac{1}{2}\hbar\omega + 2\hbar\omega\right) [a^\dagger |E_1\rangle] \quad (17.19)$$

and we could call the new eigenvector:  $|E_2\rangle = a^\dagger |E_1\rangle$ . We could keep doing this and we will obtain the following for the  $n$ -th ket vector:

$$H |E_n\rangle = \left(\frac{1}{2}\hbar\omega + n\hbar\omega\right) |E_n\rangle \quad (17.20)$$

which leads us to the harmonic oscillator energy expression:  $E = \left(n + \frac{1}{2}\right)\hbar\omega$  (which we got earlier by solving some tedious differential equation. This new approach that we have introduced involves a lot less math (as compared to the differential equation we solved to obtain the Hermite polynomials) and we obtain the same result.

10. However, what does  $a$  do when it acts on the eigenket  $|E_0\rangle$ ? Lets see if we can answer this question. Lets assume:

$$a |E_n\rangle = \beta_n |E_{n-1}\rangle \quad (17.21)$$

where the  $\beta_n$  are to be determined. This equation also means:

$$\langle E_n | a^\dagger = \langle E_{n-1} | \beta_n^* \quad (17.22)$$

where we have written the dual space analogue of Eq. (17.21). From Eq. (17.21) and Eq. (17.22) we obtain:

$$\langle E_n | a^\dagger a |E_n\rangle = |\beta_n|^2 \langle E_{n-1} | E_{n-1}\rangle = |\beta_n|^2 \quad (17.23)$$

Using Eq. (17.4) we see that

$$\begin{aligned} \langle E_n | a^\dagger a |E_n\rangle &= \langle E_n | \frac{H}{\hbar\omega} - \frac{1}{2} |E_n\rangle \\ &= n + \frac{1}{2} - \frac{1}{2} = n \end{aligned} \quad (17.24)$$

(For this reason  $a^\dagger a$  is called the number operator.) Therefore  $\beta_n = \sqrt{n}$  and

$$a |E_n\rangle = \sqrt{n} |E_{n-1}\rangle \quad (17.25)$$

This leads to  $a |E_0\rangle = 0$ . That is the operator  $a$  “annihilates” the state  $|E_0\rangle$ . For this reason  $a$  is also called the annihilation operator. For similar reasons the operator  $a^\dagger$  is called the “creation” operator. Creation and annihilation operators are extremely important in quantum chemistry, since many advanced techniques to solve the time independent Schrödinger Equation are based on the use of these techniques. The interested reader should look at the following two references for further reading in this subject: (a) H. C. Longuet-Higgins, in Quantum Theory of Atoms

and Molecules, A TRIBUTE TO JOHN C. SLATER, Ed. P.-O-Löwdin, Academic Press 1966. p. 105. (b) Simons and Jorgensen, "Second Quantization methods in quantum chemistry".

11. Now the question:

$$a^\dagger |E_n\rangle = \alpha_n |E_{n+1}\rangle \quad (17.26)$$

and what is  $\alpha_n$ . We follow the same approach as before:

$$\langle E_n | a = \langle E_{n+1} | \alpha_n^* \quad (17.27)$$

and multiplying the two equations:

$$\langle E_n | aa^\dagger |E_n\rangle = |\alpha_n|^2 \langle E_{n+1} | E_{n+1}\rangle = |\alpha_n|^2 \quad (17.28)$$

Now using Eq. (17.5) we have  $\langle E_n | aa^\dagger |E_n\rangle = n + 1$  and therefore  $\alpha_n = \sqrt{n + 1}$ . Therefore,

$$a^\dagger |E_n\rangle = \sqrt{n + 1} |E_{n+1}\rangle \quad (17.29)$$

12. **Homework:** Use Eqs. (17.29) and (17.25) in Eq. (17.6) to confirm the eigenvalues and eigenvectors of the Harmonic oscillator.

13. In the next few pages we will see an important application of the harmonic oscillator problem, that is infra-red spectroscopy. In particular we will see that second quantization can be used to obtain *selection rules* for IR spectra with little effort.
14. One very important reason for studying the harmonic oscillator problem is vibrational spectroscopy. To a first approximation one could assume that the chemical bond is harmonic. That is when perturbed from its equilibrium position the bond tends to relax back to its original equilibrium position. As a result we could assume that a carbon-carbon bond (for example) has a spring that connects the two carbon atoms as seen in the figure below. (Note this approximation is only true at low energies. As we approach the dissociation limit the potential energy in the bond deviates substantially from the harmonic potential, as seen in the figure below.)
15. Hence for lower vibrational states, the harmonic potential should be a valid approximation and what we have derived in the previous section could be used to get the properties that one might see in vibrational spectroscopy. Lets see what we can do here.



21. In IR spectroscopy, radiation of a certain frequency is incident on the system, and response is studied and this is what leads to the “spectrum” of the molecule. In most cases, when the applied radiation is *weak*, one quantity that is very useful to calculate is the *transition dipole bracket* (which we will define below), since the response of the system is proportional to the transition dipole bracket. What this essentially means is the probability of the transition from state  $|m\rangle$  to state  $|n\rangle$  in the presence of an electromagnetic field (or light) is given by the quantity:

$$\mathcal{P}(t) \propto |\langle m | \hat{x} | n \rangle|^2 \quad (17.30)$$

Eq. (17.30) will not be derived in this class. It can be derived using time-dependent perturbation theory which we may not have time to cover. The interested reader may look at Chapter 12 of Fayer.

22. However, we note the following. The incident radiation comprises electric and magnetic fields. (We saw earlier, during the SG experiments, that light consists of mutually orthogonal electric and magnetic field vectors.) The electric field vector interacts with the “dipole operator”. In fact, the quantity  $\langle m | \hat{x} | n \rangle$  is called the transition dipole bracket. Why? It has the units of a dipole (position times a charge density). And that is why its called the transition dipole bracket. The magnitude of this elements tells us the probability of transition between states  $m$  and  $n$  in the presence of an external field.
23. Now the probability of transition from state  $|m\rangle$  to state  $|n\rangle$  in the presence of radiation is proportional to the dipole bracket.

Lets see if we can evaluate this for the harmonic oscillator and get some results for IR spectroscopy.

24. Using the definition of the creation and annihilation operators in Eqs. (17.1) and (17.2) we can write the position operator as:

$$\hat{x} = \sqrt{\frac{\hbar\omega}{2k}} (a^\dagger + a) \quad (17.31)$$

Therefore,

$$\begin{aligned} \mathcal{P}(t) &\propto |\langle m | \hat{x} | n \rangle|^2 = \frac{\hbar\omega}{2k} |\langle m | (a^\dagger + a) | n \rangle|^2 \\ &= \frac{\hbar\omega}{2k} \langle m | (a^\dagger + a) | n \rangle \langle n | (a^\dagger + a) | m \rangle \\ &= \frac{\hbar\omega}{2k} [\langle m | a^\dagger | n \rangle \langle n | a^\dagger | m \rangle + \langle m | a | n \rangle \langle n | a | m \rangle + \\ &\quad \langle m | a^\dagger | n \rangle \langle n | a | m \rangle + \langle m | a | n \rangle \langle n | a^\dagger | m \rangle] \end{aligned} \quad (17.32)$$

Now since  $[a |m\rangle = \sqrt{m} |m - 1\rangle]$  and  $[a^\dagger |m\rangle = \sqrt{m + 1} |m + 1\rangle]$ , the first and second term in the last equation above must be zero.

Therefore:

$$\begin{aligned} \mathcal{P}(t) &\propto \frac{\hbar\omega}{2k} [\langle m | a^\dagger | n \rangle \langle n | a | m \rangle + \langle m | a | n \rangle \langle n | a^\dagger | m \rangle] \\ &= \frac{\hbar\omega}{2k} [|\langle m | a^\dagger | n \rangle|^2 + |\langle m | a | n \rangle|^2] \\ &= \frac{\hbar\omega}{2k} [(n + 1)|\langle m | n + 1 \rangle|^2 + n|\langle m | n - 1 \rangle|^2] \end{aligned} \quad (17.33)$$

which can only be non-zero when  $m = n + 1$  or  $m = n - 1$ .

25. *This means the transition in IR spectroscopy is allowed only between eigenvalues that differ by 1, if the harmonic approximation is valid. This a vibrational spectrum selection rule.* Now we have seen earlier that the harmonic approximation is valid for the lower vibrational states, but not for the higher vibrational states (close to dissociation). Hence these selection rules are not valid at higher vibrational states. However, it turns out in practice that even at higher states the major contribution does come from the lines that differ by one quanta!!
26. **Homework:** Using the approach due to Dirac (ie the creation and annihilation operators), derive expressions for  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle p \rangle$  and  $\langle p^2 \rangle$  for the harmonic oscillator. Use this to obtain the uncertainty product  $\Delta x \Delta p$ . Comment on your result.

**27. Homework on Frank-Condon Factors:** By solving the electronic Schrödinger Equation, ground and excited electronic states can be obtained at various nuclear configuration like the figure presented in class. In addition, the figure also shows the vibrational levels.

Solving for vibrational levels using the nuclear Schrödinger Equation after solving the electronic Schrödinger Equation can get very complicated but for the smallest of systems. Due to this reason, the vibrational states are assumed to exist on a Harmonic oscillator potential located at the minimum of the corresponding electronic state as in the figure below. The force constant for the harmonic oscillator assumes a value such that the curvature of the original surface is identical at the bottom of the potential (as you can see from the figure).

This is only an approximation as you can see, and will work well for the low-lying vibrational levels of each electronic state.

While doing optical spectroscopy what happens is the electrons are excited from the ground electronic state to the excited electronic state as represented by the arrow in the figure. Clearly the vibrational level in the excited electronic state where the electron gets into is important. Here's where the Frank-Condon Factors come in. These represent the probability of such transitions. The transition from the  $i$ -th vibrational level in the ground electronic state to the  $j$ -th vibrational level in the first excited electronic state is given by the inner product of the vibrational states  $\langle \psi_0^i | \psi_1^j \rangle$ , where  $|\psi_0^i\rangle$  represents the  $i$ -th vibrational level in the ground electronic state, and  $|\psi_1^j\rangle$  represents the  $j$ -th vibrational

level in the first excited electronic state.

- (a) Using the definition of *the creation operator* and the form of the lowest eigenstate of the Harmonic oscillator:

$$\left\{ \exp \left[ -\frac{\sqrt{mk}}{2\hbar} (x - x_0)^2 \right] \right\}, \quad (17.34)$$

show that the  $n$ -th vibrational state of a Harmonic oscillator is:

$$\begin{aligned} \psi_0^n &= \frac{1}{\sqrt{n!}} (a^\dagger)^n \exp \left[ -\frac{\sqrt{mk_0}}{2\hbar} (x - x_0)^2 \right] \\ &= \frac{1}{\sqrt{n!}} \left( \frac{m\omega_0}{2\hbar} \right)^{n/2} \left( x - \frac{\hbar}{m\omega_0} \frac{\partial}{\partial x} \right)^n \exp \left[ -\frac{\sqrt{mk_0}}{2\hbar} (x - x_0)^2 \right] \end{aligned} \quad (17.35)$$

$x_0$  is the equilibrium distance and  $k_0 = m\omega_0^2$  is the force constant of the Harmonic oscillator. Note: Using the creation operator will significantly reduce your effort.

- (b) Using Eq. (17.35) write down an expression for the Frank-Condon factor  $\langle \psi_0^i | \psi_1^j \rangle$ , assuming that the equilibrium positions and force constants are different in the ground and excited states, that is  $\{x_0, \omega_0, k_0\}$  for the ground electronic state and  $\{x_1, \omega_1, k_1\}$  for the excited electronic state. You do not need to go through the whole integration, just write down the starting expression and explain in words how you would integrate it, if you were asked to integrate it by hand.
- (c) Comment on how your derivation would simplify (greatly) if the equilibrium positions and force constants were the same in the ground and excited states.