Chapter 6
The Harmonic Oscillator

Turning Points, $A$, $-A$

Stretch spring, let go. Mass, $m$, oscillates back and forth.

Hooke's Law: $F = -kx$  \hspace{1cm} \text{linear restoring force}

-force \hspace{3cm} \text{spring constant}

$F = ma$

$m\ddot{x} = -kx$

$\frac{d^2 x(t)}{dt^2} = -\left(\frac{k}{m}\right)x(t)$

$x(t) = A \sin\left(\frac{k}{m}\right)^{1/2} t$

Harmonic oscillator - oscillates sinusoidally.

A is how far the spring is stretched initially.

At the turning points, $A$, $-A$, motion stops.

All energy is potential energy.
Potential is Parabolic

\[ F = -\frac{\partial V(x)}{\partial x} \]

\[ V(x) = \int k x \, dx = \frac{1}{2} k x^2 \]

\[ k = 4\pi^2 m\nu^2 = m\omega^2 \]

Energy of oscillator is

\[ E = \frac{1}{2} k A^2 \quad A - \text{classical turning point.} \]

\( A \) can take on any value. Energy is continuous, continuous range of values.
Quantum Harmonic Oscillator

Simplest model of molecular vibrations

Bonds between atoms act as "springs".
Near bottom of molecular potential well,
molecular potential approximately parabolic

Harmonic Oscillator.
Potential \[ V(x) = \frac{1}{2} k x^2 \]

Turning point
Kinetic energy zero; potential energy max.

Classical particle can never be past turning point.

Particle can be stationary at bottom of well, know position, \( x = 0 \); know momentum, \( p = 0 \).

\[ \therefore \Delta x \Delta p = 0 \]

This can't happen for Q.M. harmonic oscillator. Uncertainty Principle indicates that minimum Q.M. H.O. energy \( \neq 0 \)
One Dimensional Quantum Harmonic Oscillator
in the Schrödinger Representation

\[ H|\psi\rangle = E|\psi\rangle \]

\[(H - E)|\psi\rangle = 0 \]

\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \quad \text{Schrödinger Representation} \]

\[ \text{kinetic energy} \quad \text{potential energy} \]

\[ \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} \left[ E - 2\pi^2 mv^2 x^2 \right] \psi(x) = 0. \quad \text{Substitute } H \text{ and definition of } k. \]

\[ \alpha = 2\pi mv / \hbar \]

\[ \lambda = \frac{2mE}{\hbar^2} \quad \text{Define} \]

\[ \frac{d^2\psi(x)}{dx^2} + \left( \lambda - \alpha^2 x^2 \right) \psi(x) = 0 \]

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Find $\psi(x)$

$$\frac{d^2\psi(x)}{d\,x^2} + \left(\lambda - \alpha^2 x^2\right)\psi(x) = 0$$

Good from $-\infty \leftrightarrow \infty$.

Must obey Born Conditions

1. finite everywhere
2. single valued
3. continuous
4. first derivative continuous

Use polynomial method

1. Determine $\psi(x)$ for $x \to \infty$
2. Introduce power series to make the large $x$ solution correct for all $x$. 
\[ \frac{d^2 \psi (x)}{dx^2} + (\lambda - \alpha^2 x^2) \psi (x) = 0 \]

For very large \( x \), as \( x \) goes to infinity.

\[ \alpha^2 x^2 \gg \lambda \quad \quad \lambda = \frac{2mE}{\hbar^2} \]

Therefore, \( \lambda \) can be dropped.

Try

\[ \psi = e^{\pm \frac{\alpha}{2} x^2} \]

Then,

\[ \frac{d^2 \psi}{dx^2} = \alpha^2 x^2 e^{\pm \frac{\alpha}{2} x^2} \pm \alpha e^{\pm \frac{\alpha}{2} x^2} \]

This is negligible compared to the first term as \( x \) goes to infinity.
Two solutions

\[ e^{-\frac{\alpha}{2}x^2} \quad e^{\frac{\alpha}{2}x^2} \]

This is O.K. at \( x = \pm \infty \) This blows up at \( x = \pm \infty \)

Not finite everywhere.

Therefore, large \( x \) solution is

\[ \psi(x) = e^{-\frac{\alpha}{2}x^2} \]

For all \( x \)

\[ \psi(x) = e^{-\frac{\alpha}{2}x^2} f(x) \]

Must find this.
\[ \psi(x) = e^{-\frac{\alpha}{2} x^2} f(x) \]

Need second derivative in Schrödinger equation

\[
\frac{d^2 \psi(x)}{dx^2} = e^{-\frac{\alpha}{2} x^2} \left( \alpha^2 x^2 f - \alpha f - 2 \alpha x f' + f'' \right)
\]

With \[ f' = \frac{df}{dx} \quad \text{and} \quad f'' = \frac{d^2 f}{dx^2} \]

Substitute \[ \frac{d^2 \psi(x)}{dx^2} \text{ and } \psi(x) \] into the original equation

\[
\frac{d^2 \psi(x)}{dx^2} + \left( \lambda - \alpha^2 x^2 \right) \psi(x) = 0
\]

and divide by \[ e^{-\frac{\alpha}{2} x^2} \] gives

\[ f'' - 2 \alpha x f' + (\lambda - \alpha) f = 0 \]

Equation only in \( f \).
Solve for \( f \) and have \( \psi(x) \).
divide by $\alpha$

$$\frac{1}{\alpha} f'' - 2x f' + \left( \frac{\lambda}{\alpha} - 1 \right) f = 0.$$ 

substitute

$$\gamma = \sqrt{\alpha} \ x$$

$$f(x) = H(\gamma)$$

Gives

$$\frac{d^2 H(\gamma)}{d \gamma^2} - 2\gamma \frac{d H(\gamma)}{d \gamma} + \left( \frac{\lambda}{\alpha} - 1 \right) H(\gamma) = 0. \quad \text{Hermite's equation}$$

Substitute series expansion for $H(\gamma)$

$$H(\gamma) = \sum_{\nu} a_{\nu} \gamma^\nu = a_0 \gamma^0 + a_1 \gamma^1 + a_2 \gamma^2 + a_3 \gamma^3 + \cdots$$

$$\frac{dH(\gamma)}{d \gamma} = \sum_{\nu} \nu a_{\nu} \gamma^{\nu-1} = a_1 \gamma^0 + 2a_2 \gamma^1 + 3a_3 \gamma^2 + \cdots$$

$$\frac{d^2 H}{d \gamma^2} = \sum_{\nu} \nu (\nu - 1) a_{\nu} \gamma^{\nu-2} = 2a_2 \gamma^0 + 6a_3 \gamma^1 + \cdots$$
\[
\frac{d^2 H(\gamma)}{d \gamma^2} - 2 \gamma \frac{d H(\gamma)}{d \gamma} + \left( \frac{\lambda}{\alpha} - 1 \right) H(\gamma) = 0. \\
\text{substitute in series}
\]

\[
2a_2 \gamma^0 + 6a_3 \gamma^1 + 12a_4 \gamma^2 + 20a_5 \gamma^3 + \cdots
\]

\[
-2a_1 \gamma^1 - 4a_2 \gamma^2 - 6a_3 \gamma^3 - \cdots
\]

\[
+ \left( \frac{\lambda}{\alpha} - 1 \right) a_0 \gamma^0 + \left( \frac{\lambda}{\alpha} - 1 \right) a_1 \gamma^1 + \left( \frac{\lambda}{\alpha} - 1 \right) a_2 \gamma^2 + \left( \frac{\lambda}{\alpha} - 1 \right) a_3 \gamma^3 + \cdots = 0.
\]

The sum of these infinite number of terms in all powers of \( \gamma \) equals 0.

In order for the sum of all the terms in this expression to vanish identically for any \( \gamma \), the coefficients of the individual powers of \( \gamma \) must vanish separately.

To see this consider an unrelated simpler equation.

\[
a_5 x^5 + a_4 x^4 + a_3 x^3 + a_2 x^2 + a_1 x + a_0 = 0
\]

Fifth degree equation. For a given set of the \( a_i \), there will be 5 values of \( x \) for which this is true. However, if you know this is true for any value of \( x \), then the \( a_i \) all must be zero.
\[ 2a_2 + \left( \frac{\lambda}{\alpha} - 1 \right) a_0 = 0 \quad \left[ \gamma^0 \right] \]

\[ 6a_3 + \left( \frac{\lambda}{\alpha} - 3 \right) a_1 = 0 \quad \left[ \gamma^1 \right] \]

\[ 12a_4 + \left( \frac{\lambda}{\alpha} - 5 \right) a_2 = 0 \quad \left[ \gamma^2 \right] \]

\[ 20a_5 + \left( \frac{\lambda}{\alpha} - 7 \right) a_3 = 0 \quad \left[ \gamma^3 \right] \]

In general

\[(\nu+1)(\nu+2)a_{\nu+2} + \left( \frac{\lambda}{\alpha} - 1 - 2\nu \right) a_{\nu} = 0 \quad \nu \text{ is an integer. Index in the expansion.} \]

\[ a_{\nu+2} = -\frac{\left( \frac{\lambda}{\alpha} - 2\nu - 1 \right)}{(\nu+1)(\nu+2)} a_{\nu} \]

Even and odd series.
Pick \( a_0 \) (\( a_1 = 0 \)), get all even coefficients.
Pick \( a_1 \) (\( a_0 = 0 \)), get all odd coefficients.
Normalization set \( a_0 \) and \( a_1 \) values.

Recursion Formula
Have expression in terms of series that satisfy the diff. eq.

But not good wavefunction.

Blows up for large $|x|$ if infinite number of terms. (See book for proof.)

$$\psi(\gamma) = e^{\frac{-\gamma^2}{2}} H(\gamma)$$

For infinite number of terms and large $|x|$. ($\gamma = \sqrt{\alpha \ x}$)

blows up

Unacceptable as a wavefunction.
Quantization of Energy

If there are a finite number of terms in the series for $H(\gamma)$, wavefunction does not blow up. Goes to zero at infinity.

$$e^{-\gamma^2/2} \gamma^n$$ The exponential goes to zero faster than $\gamma^n$ blows up.

To make series finite, truncate by choice of $\lambda$.

$$\lambda = \alpha(2n + 1) \quad n \text{ is an integer.}$$

Then, because

$$a_{\nu+2} = -\left(\frac{\lambda}{\alpha} - 2\nu - 1\right) \frac{a_\nu}{(\nu+1)(\nu+2)}$$

with $a_0$ or $a_1$ set equal to zero (odd or even series), series terminates after

$$\nu = n \quad \text{a finite number of terms.}$$
Any value of $\lambda$ with

$$\lambda = (2n + 1)\alpha$$

is O.K. Any other value of $\lambda$ is no good.

Therefore,

$$\lambda = \frac{2mE}{\hbar^2} = (2n + 1) \frac{2\pi mv}{\hbar}$$

Solving for $E$

$$E_n = \left( n + \frac{1}{2} \right) \hbar \nu$$

$n$ is the quantum number

$n = 0 \quad E_0 = 1/2 \hbar \nu$

Lowest energy, not zero. Called zero point energy.

Energy levels equally spaced by $\hbar \nu$. 
Energy Levels

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \nu \]

Wavefunctions

\[ \psi_n (x) = N_n e^{-\frac{\gamma^2}{2}} H_n (\gamma) \]

\[ \gamma = \sqrt{\alpha} x \quad \alpha = 2\pi m \nu / \hbar \]

\[ N_n = \left\{ \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \frac{1}{2^n n!} \right\}^{\frac{1}{2}} \quad \text{normalization constant} \]

Hermite Polynomials

\[ H_0 (\gamma) = 1 \gamma^0 \]

\[ H_1 (\gamma) = 2 \gamma \]

\[ H_2 (\gamma) = 4\gamma^2 - 2\gamma^0 \]

\[ H_3 (\gamma) = 8\gamma^3 - 12\gamma \]

\[ H_4 (\gamma) = 16\gamma^4 - 48\gamma^2 + 12\gamma^0 \]

\[ H_5 (\gamma) = 32\gamma^5 - 160\gamma^3 + 120\gamma \]

\[ H_6 (\gamma) = 64\gamma^6 - 480\gamma^4 + 720\gamma^2 - 120\gamma^0 \]
Lowest state \( n = 0 \)

\[
\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^\frac{1}{4} e^{-\frac{\alpha}{2}x^2} = \left(\frac{\alpha}{\pi}\right)^\frac{1}{4} e^{-\frac{x^2}{2}}
\]

This is a Gaussian. Minimum uncertainty.

Classical turning points

\[
\frac{1}{2} kx^2 = \frac{1}{2} \hbar \nu
\]

\[
\therefore x^2 = \frac{\hbar \nu}{k}
\]

\[
x = \pm \sqrt{\hbar \nu / k} = \pm \gamma
\]

classical turning points - wavefunction extends into classically forbidden region.
More wavefunctions - larger \( n \), more nodes
Probability for $n = 10$

Classical turning points

$\sim \gamma = \pm 4.6$

Time classical oscillator spends as a function of position.

Looks increasingly classical.

For large object, nodes so closely spaced because $n$ very large that can't detect nodes.
Dirac Approach to Q.M. Harmonic Oscillator

Very important in theories of vibrations, solids, radiation

$$H = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

Want to solve eigenkets, normalized

$$\langle H | E \rangle = E \langle E \rangle$$

We know commutator relation

$$[x, P] = i \hbar 1$$

To save a lot of writing, pick units such that

$$m = 1 \quad k = 1 \quad \hbar = 1$$

In terms of these units

$$H = \frac{1}{2} (P^2 + x^2)$$

$$[x, P] = i 1$$

identity operator
Define operators

\[ a = \frac{i}{\sqrt{2}}(P - i x) \quad \quad a^+ = \frac{1}{i\sqrt{2}}(P + i x) \]

\[ a^+ = \bar{a} \quad \quad a^+ \text{ is the complex conjugate (adjoint) of } a \text{ since } P \text{ and } x \text{ are Hermitian.} \]

Then

\[ aa^+ = \frac{1}{2}[(P - i x)(P + i x)] \]

\[ = \frac{1}{2}[P^2 - i x P + i P x + x^2] \]

\[ = \frac{1}{2}[P^2 - i(xP - P x) + x^2] \]

\[ = \frac{1}{2}[P^2 + x^2] - \frac{i}{2}[x, P] \]

\[ \therefore \quad aa^+ = H + \frac{1}{2} \]
\[ a a^+ = H + \frac{1}{2} \]

Similarly

\[ a^+ a = \frac{1}{2} [P^2 + i(xP - Px) + x^2] \]

\[ a^+ a = H - \frac{1}{2} \]

Therefore

\[ H = \frac{1}{2} (a a^+ + a^+ a) \quad \text{Very different looking from Schrödinger Hamiltonian.} \]

and

\[ [a, a^+] = 1 \]

Can also show

\[ [a, H] = a \quad [a^+, H] = -a^+ \]
Consider $|E\rangle$; eigenkets of $H$, normalized.

$$a|E\rangle = |Q\rangle$$

$$\langle Q | = \langle E | a = \langle E | a^+$$

$$\langle Q | Q \rangle \geq 0 \quad \text{scalar product of vector with itself}$$

$$\langle Q | Q \rangle = 0 \quad \text{only if} \quad |Q\rangle = 0$$

We have

$$\langle Q | Q \rangle = \langle E | a^+ a | E \rangle \geq 0.$$ 

Then

$$\langle E | a^+ a | E \rangle = \langle E | H - \frac{1}{2} 1 | E \rangle = (E - \frac{1}{2}) \langle E | E \rangle \geq 0$$

Therefore, $E \geq \frac{1}{2}$ normalized, equals 1
Now consider \( aH |E\rangle = E a |E\rangle \) eigenket of \( H \)

commutator

\[
[a, H] = a H - H a = a
\]

rearrange

\[
a H = H a + a
\]

Then,

\[
(H a + a) |E\rangle = a H |E\rangle = E a |E\rangle
\]

\[
H a |E\rangle + a |E\rangle = E a |E\rangle
\]

transpose

\[
H a |E\rangle = E a |E\rangle - a |E\rangle
\]

factor

\[
H [a |E\rangle] = (E - 1) [a |E\rangle]
\]

these are same

\( a |E\rangle \) is some ket.

Operate \( H \) on ket, get same ket back times number.

\[
[a |E\rangle] \text{ is eigenket with eigenvalue, } E - 1.
\]

\[
H [a |E\rangle] = (E - 1) [a |E\rangle]
\]

eigenvalue eigenket

\( a |E\rangle = |E - 1\rangle \)

Label ket with eigenvalue.

Maybe number multiplying.

Direction defines state, not length.
\( a \) is a lowering operator. It gives a new eigenvector of \( H \) with one unit lower energy.

\[
\begin{align*}
\alpha |E\rangle &= |E - 1\rangle \\
\alpha^2 |E\rangle &= |E - 2\rangle \\
\alpha^3 |E\rangle &= |E - 3\rangle \\
&\vdotswithin{=} \\
\end{align*}
\]

Each application gives a new ket with one unit lower energy.

Could keep doing this indefinitely, but

\[
E \geq \frac{1}{2}
\]

Therefore, at some point we have a value of \( E, \) call it \( E_0, \)
such that if we subtract 1 from it

\[
E_0 - 1 < \frac{1}{2}
\]

But \( E_0 - 1 \) can't be \( < 1/2. \) Therefore \( \alpha |E_0\rangle = 0 \)

For eigenvector \( |E_0\rangle \)

\[
\begin{align*}
\alpha^+ \left[ \alpha |E_0\rangle \right] &= (H - \frac{1}{2} 1) |E_0\rangle \\
&= (E_0 - \frac{1}{2}) |E_0\rangle = 0 \\
E_0 &= \frac{1}{2} \\
\end{align*}
\]

\( E_0 = \frac{1}{2} \) not zero in conventional units

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Raising Operator

\[ a^+ \left[ H | E \rangle \right] = E a^+ | E \rangle \]

\[ a^+ \left[ H | E \rangle \right] = (H a^+ - a^+) | E \rangle \] using the commutator

\[ (H a^+ - a^+) | E \rangle = E a^+ | E \rangle \]

rearranging, operating, and factoring as before

\[ H \left[ a^+ | E \rangle \right] = (E + 1) \left[ a^+ | E \rangle \right] \]

These are the same.

Therefore, \[ a^+ | E \rangle \] is an eigenket of \( H \) with eigenvalue \( E + 1 \).

\[ a^+ | E \rangle = | E + 1 \rangle \]

\( a^+ \) takes state into new state, one unit higher in energy.

It is a raising operator.
$|E_0\rangle$ is the state of lowest energy with eigenvalue (energy) 1/2. Apply raising operator repeatedly. Each application gives state higher in energy by one unit.

$H|E_0\rangle = \frac{1}{2} |E_0\rangle$

eigenvalue, one unit higher in energy

$H\left[a^+ |E_0\rangle\right] = \frac{3}{2} |E_0 + 1\rangle$

$H\left[a^{+2} |E_0\rangle\right] = \frac{5}{2} |E_0 + 2\rangle$

$H\left[a^{+3} |E_0\rangle\right] = \frac{7}{2} |E_0 + 3\rangle$

$E = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$

$E_n = \left(n + \frac{1}{2}\right)$

With normal units $E_n = \left(n + \frac{1}{2}\right)\hbar\nu$ Same result as with Schrödinger Eq.
Schrödinger vs. Dirac Approaches

1. Hamiltonian and method of solution, mathematically very different, but eigenvalues the same.

2. Dirac, only needed Hamiltonian and commutator, no auxiliary Born Conditions.

3. No wave functions in Dirac approach. Wave functions intermediate step in Schrödinger method. Not necessary. Not real in sense not observables, but can be useful in qualitative understanding.
Eigenkets labeled with energy

\[ |E = n + \frac{1}{2} \rangle \]

Can relabel kets with quantum number

\[ |E = n + \frac{1}{2} \rangle = |n \rangle \quad \text{Take } |n \rangle \text{ to be normalized.} \]

Raising and Lowering operators

\[ a^+ |n \rangle = \beta_n |n+1 \rangle \quad a |n \rangle = \alpha_n |n-1 \rangle \]

\[ \beta_n = \sqrt{n+1} \quad \alpha_n = \sqrt{n} \quad \text{numbers multiply ket when raise or lower} \]

\[ a^+ |n \rangle = \sqrt{(n+1)} |n+1 \rangle \quad a |n \rangle = \sqrt{n} |n-1 \rangle \]

Will derive these below.
Consider operator

\[ a^+ a \]

operating on \( |n\rangle \)

\[
\begin{aligned}
    a^+ a |n\rangle &= a^+ \sqrt{n} |n - 1\rangle \\
    &= n |n\rangle 
\end{aligned}
\]

Therefore

\[
\begin{aligned}
    a^+ a |n\rangle &= n |n\rangle 
\end{aligned}
\]

\( |n\rangle \) is an eigenket of operator \( a^+ a \) with eigenvalue \( n \).

\( a^+ a \) number operator. Eigenvalue – quantum number

Important in Quantum Theory of Radiation and Solids

\( a^+ \) and \( a \) called creation and annihilation operators.

Number operator gives number of photons in radiation field or number of phonons (quantized vibrations of solids) in crystal.
Using the occupation number representation with normal units

$$H = \frac{1}{2} \hbar \omega (a a^+ + a^+ a)$$

$$\omega = 2 \pi \nu = (k / m)^{1/2}$$

Consider $H |n\rangle$

$$H |n\rangle = \frac{1}{2} \hbar \omega (a a^+ |n\rangle + a^+ a |n\rangle)$$

$$= \frac{1}{2} \hbar \omega (a(n+1)^{1/2} |n+1\rangle + a^+ n^{1/2} |n-1\rangle)$$

$$= \frac{1}{2} \hbar \omega \left( (n+1)^{1/2} (n+1)^{1/2} |n\rangle + n^{1/2} n^{1/2} |n\rangle \right)$$

$$= \frac{1}{2} \hbar \omega (2n+1) |n\rangle$$

$$= \hbar \omega \left( n + \frac{1}{2} \right) |n\rangle = \left( n + \frac{1}{2} \right) \hbar \nu |n\rangle$$

Therefore, $|n\rangle$ are eigenkets of $H$ with eigenvalues $\left( n + \frac{1}{2} \right) \hbar \omega$. 

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Units in the raising and lowering operators

\[
a = \frac{i}{(2\hbar \omega)^{1/2}} \left( \frac{1}{m^{1/2}} P - i k^{1/2} x \right)
\]

\[
a^+ = \frac{1}{i(2\hbar \omega)^{1/2}} \left( \frac{1}{m^{1/2}} P + i k^{1/2} x \right)
\]

Many constants. This is the reason why derivation was done in units such that \( m = 1 \quad k = 1 \quad \hbar = 1 \). Need constants and units to work problems.

\[
a = \frac{1}{(2\hbar \omega)^{1/2}} \left( \frac{i}{m^{1/2}} P + k^{1/2} x \right)
\]

\[
a^+ = \frac{1}{(2\hbar \omega)^{1/2}} \left( \frac{-i}{m^{1/2}} P + k^{1/2} x \right)
\]

Bring \( i \) inside.

Multiply top and bottom by \(-i\), and bring \(-i\) inside.

\[
(a + a^+) = \frac{1}{(2\hbar \omega)^{1/2}} \left( 2k^{1/2} x \right) = \left( \frac{2k}{\hbar \omega} \right)^{1/2} x \quad \text{Add operators, } P \text{ cancels.}
\]

\[
x = \left( \frac{\hbar \omega}{2k} \right)^{1/2} (a + a^+) \quad x \text{ in terms of raising and lowering operators.}
\]

\[
P = -i \left( \frac{\hbar m \omega}{2} \right)^{1/2} (a - a^+) \quad \text{Subtract operators, get } P \text{ in terms of raising and lowering operators.}
\]
Can use the raising and lowering operator representation to calculate any Q.M. properties of the H. O.

**Example**

\[ \langle x^4 \rangle \Rightarrow \text{for ground state, average value of } x^4 \]

\[ \langle 0 | x^4 | 0 \rangle \]

**In Schrödinger Representation**

\[ \int_{-\infty}^{\infty} \psi_0^* x^4 \psi_0 dx \]
$$x = \left( \frac{\hbar \omega}{2k} \right)^{1/2} \left( a + a^+ \right)$$

$$\langle 0 | x^4 | 0 \rangle = \left( \frac{\hbar \omega}{2k} \right)^2 \langle 0 | (a + a^+)^4 | 0 \rangle$$

**constant - C**

$$= C \left[ \langle 0 | a^4 | 0 \rangle + \langle 0 | a^3 a^+ | 0 \rangle + \langle 0 | a^2 a^+ a | 0 \rangle + \cdots 
+ \langle 0 | (a^+)^4 | 0 \rangle \right]$$

**Many terms. Must keep order correct. Operators don’t commute.**
Could write out all of the terms, but easier way.

Any term that doesn’t have same number of $a$’s and $a^+ = 0$

Example $\langle 0 | a^+ a^+ a^+ a^+ | 0 \rangle = \langle 0 | 4 \rangle$

orthogonal = 0

Any operator that starts with $a$ is zero.

$$\cdots a | 0 \rangle = 0$$

Can't lower past lowest state.

$$\langle 0 | a a^+ a^+ a | 0 \rangle = 0$$

Terms with $\langle 0 | a^+ \rangle$ are also zero because

$$a | 0 \rangle = |Q\rangle = 0$$

$$0 = \overline{|Q\rangle} = \langle Q | = \langle 0 | a^+$$
Only terms left are

\[ \langle 0 | a a^+ a a^+ | 0 \rangle \]
\[ \langle 0 | a a a^+ a^+ | 0 \rangle \]

\[
\therefore \quad \langle 0 | x^4 | 0 \rangle = \left( \frac{\hbar \omega}{2k} \right)^2 \left[ \langle 0 | a a^+ a a^+ | 0 \rangle + \langle 0 | a a a^+ a^+ | 0 \rangle \right]
\]

\[
\begin{align*}
a^+ |n \rangle &= \sqrt{n+1} |n+1 \rangle \\
a |n \rangle &= \sqrt{n} |n-1 \rangle
\end{align*}
\]

\[
\begin{align*}
\langle 0 | a a^+ a a^+ | 0 \rangle &= \langle 0 | a a^+ a | 1 \rangle \\
&= \langle 0 | a a^+ | 0 \rangle \\
&= \langle 0 | a | 1 \rangle \\
&= \langle 0 | 0 \rangle = 1
\end{align*}
\]

\[
\begin{align*}
\langle 0 | a a a^+ a^+ | 0 \rangle &= \langle 0 | a a a^+ | 1 \rangle \\
&= \langle 0 | a a | 2 \rangle \sqrt{2} \\
&= \sqrt{2} \langle 0 | a | 1 \rangle \sqrt{2} \\
&= 2 \langle 0 | 0 \rangle = 2
\end{align*}
\]

\[
\therefore \quad \langle 0 | x^4 | 0 \rangle = \frac{3 \hbar^2 \omega^2}{4 \frac{k^2}{k^2}} \quad \text{No integrals. Must be able to count.}
\]
A short optical pulse will excite many vibrational levels of the excited state potential surface.
Model Excited State Vibrational Wave Packet with H. O. States

Time dependent H. O. ket

\[ |n(t)\rangle = |n\rangle e^{-iE_n t / \hbar} \]

Superposition representing wave packet on excited surface

\[ |t\rangle = \sum_n \alpha_n |n\rangle e^{-i\omega_n t} \]

Calculate position expectation value - average position - center of packet.

\[ \langle t | x | t \rangle \]

\[ x = \left( \frac{\hbar \omega}{2k} \right)^{1/2} (a + a^+) \]

\[ \langle t | x | t \rangle = \sum_m \alpha_m^* e^{i\omega_m t} \sum_n \alpha_n e^{-i\omega_n t} \langle m | x | n \rangle \]

\[ = \sum_{m,n} \alpha_m^* \alpha_n e^{-i(\omega_n - \omega_m) t} \sqrt{\frac{\hbar \omega}{2k}} \langle m | a + a^+ | n \rangle \]
\[ \langle m | a + a^+ | n \rangle \quad \text{only non-zero} \]

if \( m = n \pm 1 \)

Then

\[ \langle t | x | t \rangle = \sqrt{\frac{\hbar \omega}{2k}} \left[ \sum_n \left\{ \alpha_{n-1}^* \alpha_n e^{-i(\omega_n - \omega_{n-1})t} \sqrt{n} + \alpha_{n+1}^* \alpha_n e^{-i(\omega_n - \omega_{n+1})t} \sqrt{n+1} \right\} \right] \]

But \( \omega_n - \omega_{n-1} = \omega \) and \( \omega_n - \omega_{n+1} = -\omega \)

\[ \Delta E = \hbar \omega \]

\[ \langle t | x | t \rangle = \sqrt{\frac{\hbar \omega}{2k}} \left[ \sum_n \left\{ \alpha_{n-1}^* \alpha_n e^{-i\omega t} \sqrt{n} + \alpha_{n+1}^* \alpha_n e^{i\omega t} \sqrt{n+1} \right\} \right] \]

This expression shows that \( \langle x \rangle \) time dependent.
Time dependence is determined by superposition of vibrational states produced by radiation field.
Simplify

Take \( n \) large so \( n > 1 \)

Also,

\[ \alpha_i = \alpha \]

Each state same amplitude in superposition for some limited set of states.

Otherwise

\[ \alpha_j = 0 \]

Using these

\[
\left< t \mid x \mid t \right> = \sqrt{\frac{\hbar \omega}{2k}} \alpha^2 \sum_n \sqrt{n} \left( e^{-i\omega t} + e^{i\omega t} \right)
\]

\[
\left< t \mid x \mid t \right> = 2\alpha^2 \sqrt{\frac{\hbar \omega}{2k}} \sum_n \sqrt{n} \cos(\omega t)
\]

Position oscillates as \( \cos(\omega t) \).
Wave packet on potential surface, modeled as a harmonic oscillator potential.

Packet moves back and forth.

$I_2$ example

Ground state excited to B state

$\lambda \sim 565$ nm
20 fs pulse $\rightarrow$ bandwidth $\sim 700$ cm$^{-1}$

Level spacing at this energy $\rightarrow \sim 69$ cm$^{-1}$

Take pulse spectrum to be rectangle and all $\alpha$ excited same within bandwidth.

States $n = 15$ to $n = 24$ excited (Could be rectangle)
\[ \text{Cos} \quad +1 \quad \text{to} \quad -1 \]

Distance traveled twice coefficient of Cos

\[ 4\alpha^2 \sqrt{\frac{\hbar \omega}{2k}} \sum_n \sqrt{n} \]

10 equal amplitude states.

\[ \alpha^2 = 0.1 \]

\[ k = \mu \omega^2 \quad \mu = 1.05 \times 10^{-22} \text{ g} \]

\[ \omega = 1.3 \times 10^{13} \text{ Hz} \]

Distance traveled = 1.06 Å.

Comparable to bond length – 2.66 Å.
NaI Photodissociation - Zewail

Potential Energy Surfaces

Potential Energy vs. Internuclear Separation (Å)

Ionic: Na⁺ + I⁻
Covalent: Na + I

NaI⁺ → [Na···I]⁺ → Na⁺ + I + Eγ

Rₓ = 6.93 Å
Every time the wave packets hit the outer potential wall, some tunneling occurs and a little puff of products, Na + I, comes out.
\( a^+ |n\rangle = \beta_n |n+1\rangle \quad a |n\rangle = \alpha_n |n-1\rangle \)

To find \( \alpha_n \) and \( \beta_n \)

\[
\langle n-1|a|n\rangle = \alpha_n \\
\langle n+1|a^+|n\rangle = \beta_n \quad \text{Take complex conjugate}
\]

\[
\langle n|a|n+1\rangle = \beta_n^* = \alpha_{n+1}
\]

Now \( \langle n|a a^+|n\rangle = (n+1) \)

because \( a a^+ = H + 1/2 \)

\[
(H + 1/2)|n\rangle = (n + 1/2 + 1/2)|n\rangle
\]

Work out

\[
\langle n|a^+ a|n\rangle = \langle n|a|n+1\rangle \beta_n \\
= \langle n|n\rangle \alpha_{n+1} \beta_n
\]

\[
\langle n|a^+ a|n\rangle = \alpha_{n+1} \beta_n = n + 1 \quad \text{from here}
\]
\( \alpha_{n+1} \beta_n = n + 1 \)

But \( \beta_n^* = \alpha_{n+1} \)

Then \( \beta_n^* \beta_n = |\beta_n|^2 = n + 1 \)

and \( \alpha_{n+1} \alpha_{n+1}^* = |\alpha_{n+1}|^2 = n + 1 \)

Therefore,

\[ |\alpha_{n+1}|^2 = |\beta_n|^2 = n + 1 \]

True if

\[ \beta_n = \sqrt{n + 1} \]

\[ \alpha_n = \sqrt{n} \]