

# Lecture: P1\_Wk1\_L6

## The Most General Inter-Molecular Force: The London Dispersion Force

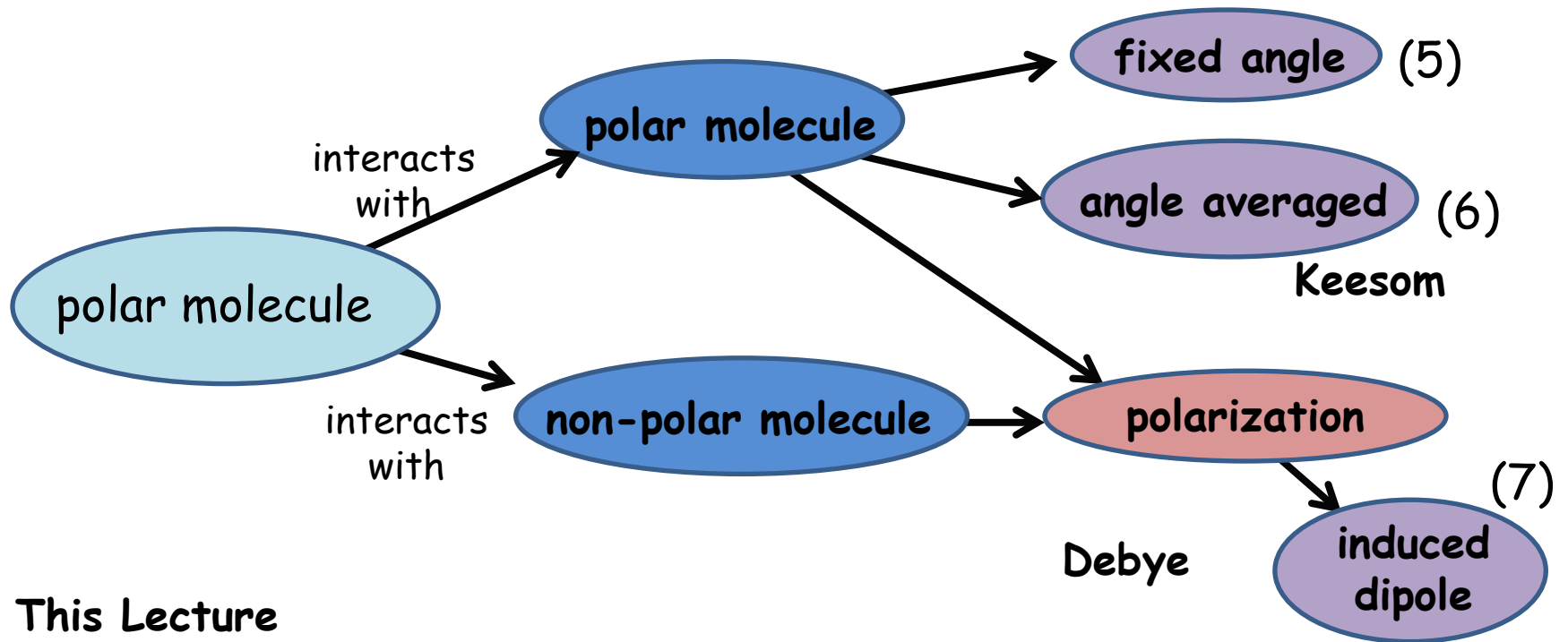
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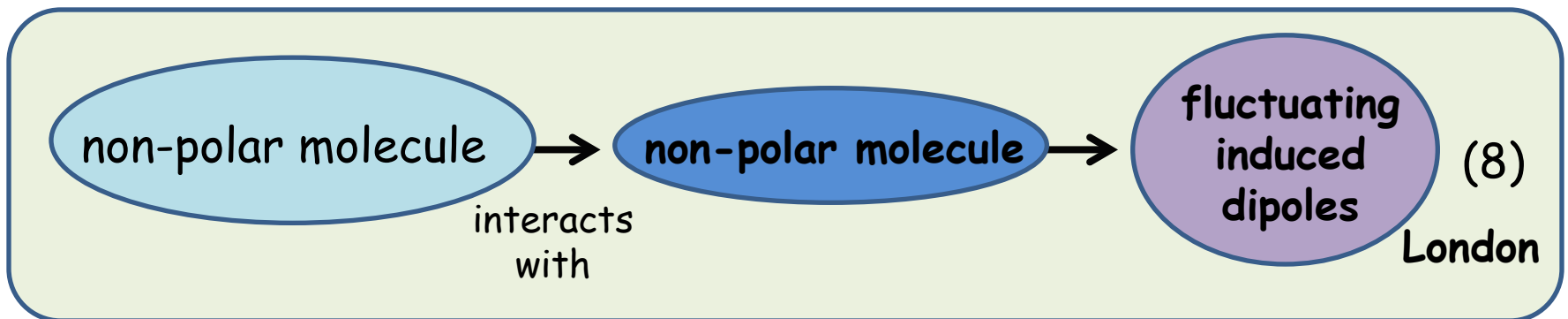
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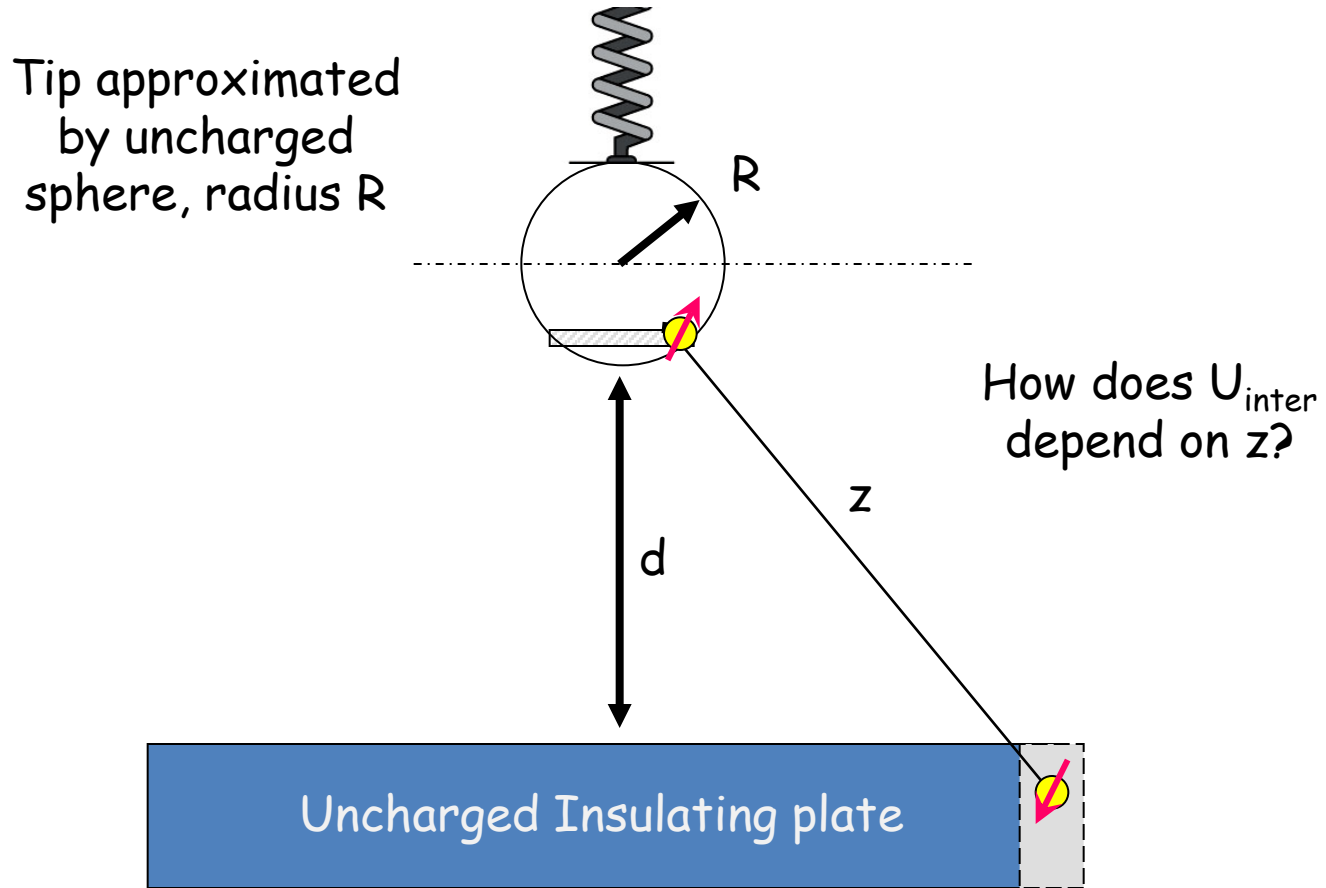
# This Lecture: Intermolecular Interactions Between Non-polar Molecules



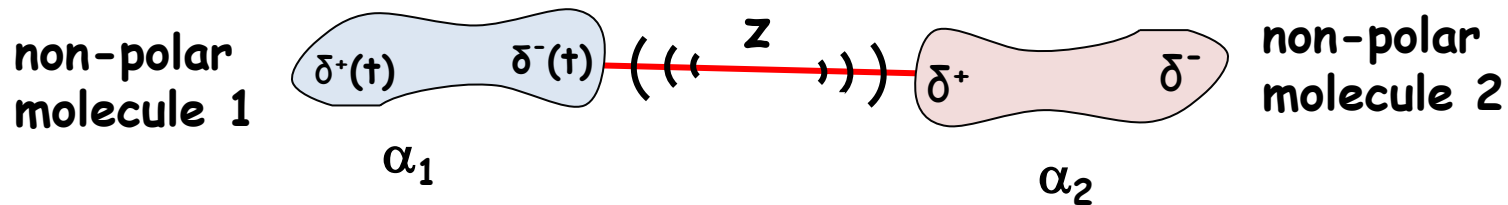
## This Lecture



# Motivation

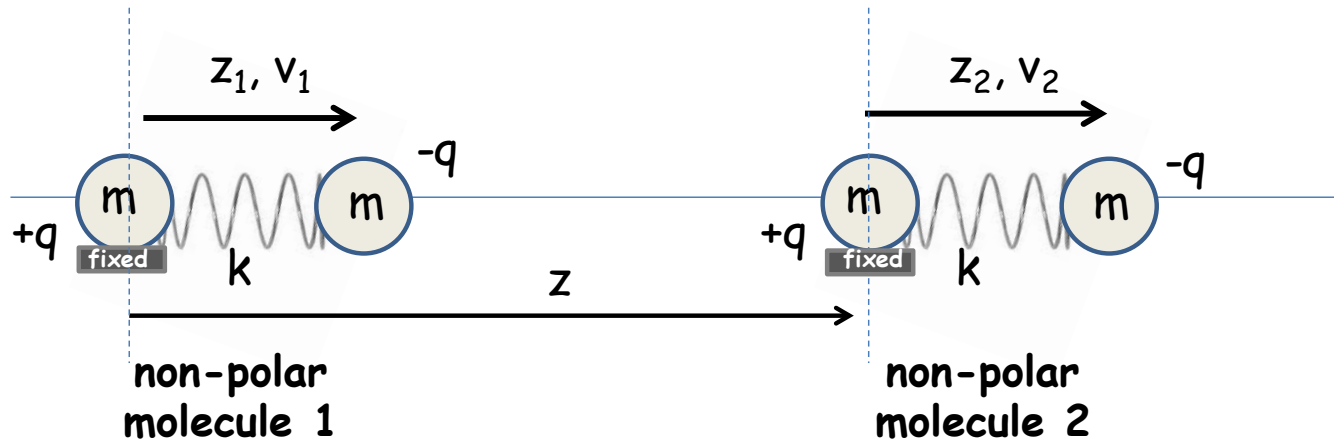


# 8. Interaction potential energy between two non-polar molecules - Dispersion Forces



- the London or Dispersion Force acts between **ALL** atoms/molecules even if they have zero permanent dipole moments
- fundamentally quantum mechanical in nature, arising from a "fluctuating dipole-induced dipole" interaction
- requires a time-correlation between fluctuating dipoles
- develop simple model for a fluctuating dipole system:

A typical fluctuation that occurs at some time:



Assume for the moment a small fluctuation in molecule 1 will induce a fluctuation in molecule 2. Model the fluctuation as a particle trapped in a parabolic well. The confining potential can be described as

$$U_1(z) = \frac{1}{2}kz_1^2 = m\omega_o^2z_1^2 \quad \text{and} \quad U_2(z) = \frac{1}{2}kz_2^2 = m\omega_o^2z_2^2.$$

Because the two oscillators are uncoupled, Schrödinger's equation reduces to two separate equations

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_1^2} \right] \Psi_1 + \frac{1}{2}m\omega_o^2z_1^2\Psi_1 = E_1\Psi_1$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_2^2} \right] \Psi_2 + \frac{1}{2}m\omega_o^2z_2^2\Psi_2 = E_2\Psi_2$$

Under these circumstances, it is well known that the allowed energy eigenvalues are

$$E_1 = \left( n + \frac{1}{2} \right) \hbar\omega_o \quad \text{and} \quad E_2 = \left( n' + \frac{1}{2} \right) \hbar\omega_o; \quad n, n' = 0, 1, 2, \dots; \quad \omega_o = \sqrt{\frac{k}{m}}$$

When the fluctuation in the molecule involves a charge, the situation changes because there is now an electrostatic interaction term given by

$$U_{electr}(z) = \frac{1}{4\pi\epsilon_o} \left[ \frac{q^2}{z} - \frac{q^2}{z+z_2} - \frac{q^2}{z-z_1} + \frac{q^2}{(z-z_1)+z_2} \right]$$

The consequences of this interaction term is fully described in Appendix A where we show the energy of the 1-dimensional system is lowered in energy by an amount

$$\Delta U(z) = -\frac{1}{2} \hbar\omega_o \left( \left( \frac{1}{4\pi\epsilon_o} \frac{q^2}{k} \right)^2 \right) \frac{1}{z^6}$$

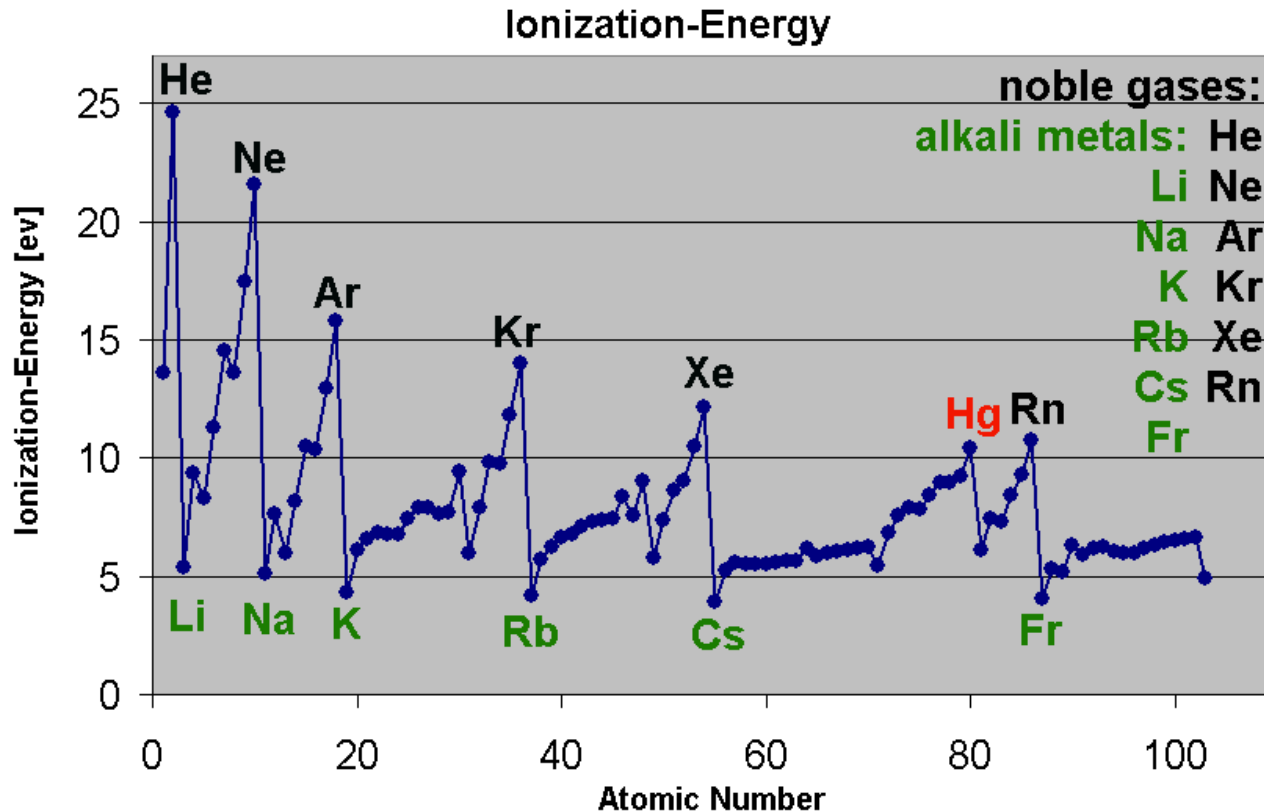
This result can be further developed (see Appendix A) for two similar molecules in 3-dimensions, embedded in a dielectric with dielectric constant  $\kappa$ :

$$U_{London}(z) = -\frac{3}{2} \frac{\alpha_o^2 I}{(4\pi\kappa\epsilon_o)^2} \frac{1}{z^6} = -\frac{C_L}{z^6}$$

where  $I$  is the ionization energy of the atom/molecule and  $\alpha_o$  is the polarizability of the atom/molecule under consideration.

For dissimilar molecules with ionization energies  $I_1$  and  $I_2$  and polarizabilities  $\alpha_{o,1}$  and  $\alpha_{o,2}$

$$U_{London}(z) = -\frac{3}{2} \frac{\alpha_{o1}\alpha_{o2}}{(4\pi\kappa\epsilon_o)^2} \left( \frac{I_1 I_2}{I_1 + I_2} \right) \frac{1}{z^6} = -\frac{C'_L}{z^6}$$



Source: [http://en.wikipedia.org/wiki/Ionization\\_energy](http://en.wikipedia.org/wiki/Ionization_energy)

# Dispersion Forces: State of the Art Electronic-structure Calculation

Full QM treatment of many-electron, non-covalent vdW interactions

Two main approaches: Hartree-Fock (HF) and Kohn-Sham density-functional theory (DFT)

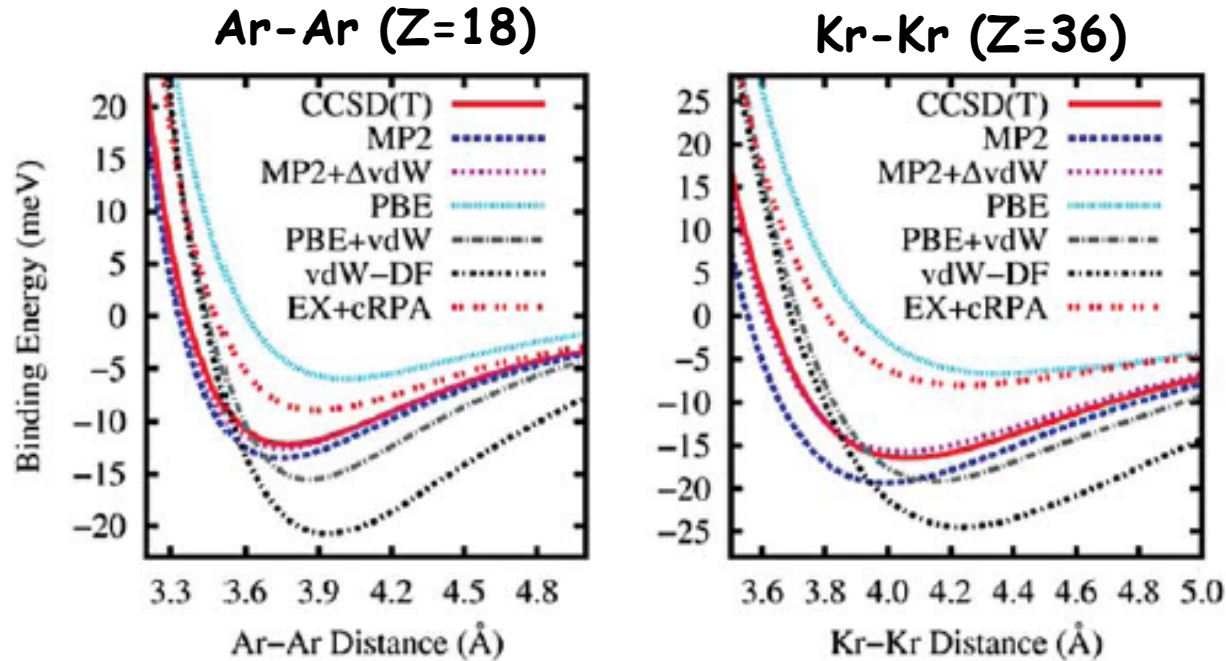


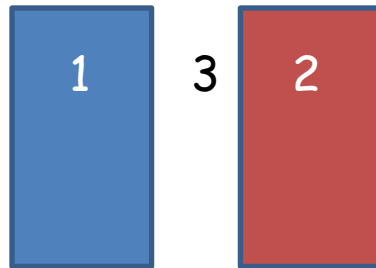
Figure 1. Performance of different approximate electronic structure methods for the description of the binding-energy curves of (a) argon (Ar) and (b) krypton (Kr) dimers. The reference results are given by CCSD(T)—coupled cluster method with single, double, and perturbative triple electron excitations. See Tables I and II for a detailed explanation of different electronic structure methods.<sup>14,20,24</sup>

Limitations: HF - accurate calculations only feasible for ~50 light atoms  
DFT - system with "thousands" of atoms (SIESTA)



The above discussion focuses mainly on atoms & molecules. Any modifications required for solids?

**Lifshitz Theory** - treats solids as continuous materials with BULK properties - macroscopic (condensed matter) treatment



- ionization energy  $I$  replaced by **frequency dependent** dielectric constant  $\epsilon(i\omega)$
- polarizability  $\alpha$  replaced by **static** dielectric constant  $\epsilon$

**More Later: see P1\_Wk2\_L1**

## 8. Dispersion Forces - comments

- The ability of fluctuating molecular dipoles to attract one another depends strongly on the frequency of the fluctuations in electron density - two transiently induced dipoles will attract each other only if their frequencies nearly match (are equal or multiples of one another). Quantities that vary with frequency are said to exhibit dispersion - hence the name **Dispersion Force, Dispersion Energy = vdW Force, vdW Energy**.
- Extensions to frequency dependent polarizations by McLachlan (1963)
- As  $z$  increase ( $>100\text{nm}$ ), the time for fluctuating dipole electric fields to reach a second atom/molecule must be taken into account. This is known as the Casimir interaction and a proper accounting of the retardation effects gives a power law dependence that varies as  $z^{-7}$ .
- Casimir-Polder force is a generalization to include finite conductivity

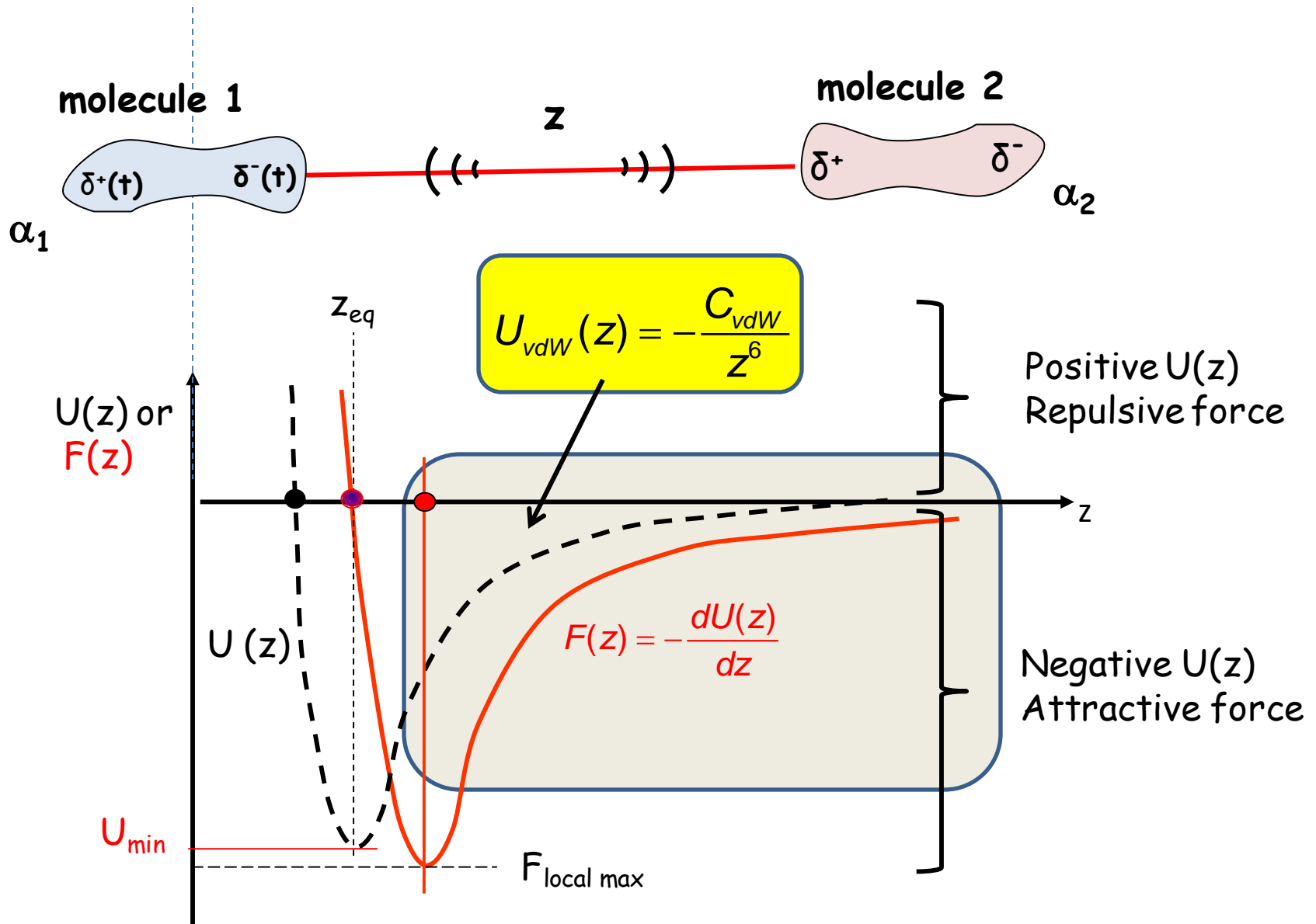
# Summary - van der Waals Forces

The van der Waals force is the sum of three different components of the electrostatic interaction between molecules: orientation, induction, and dispersion. Each electrostatic interaction produces a potential energy that varies as  $1/z^6$ , where  $z$  is the separation

- **Orientation or Keesom Force** is the angle-averaged dipole-dipole interaction between two polar molecules.
- **Debye Force** is the angle averaged dipole-induced dipole interaction between a polar and non-polar molecule
- **The London or Dispersion force** acts between all molecules with non-zero polarizability

$$\begin{aligned}
 U_{vdW}(z) &= U_{Keesom}(z) + U_{Debye}(z) + U_{London}(z) \\
 &= -\frac{2}{3} \frac{1}{k_B T} \frac{p_1^2 p_2^2}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6} - \frac{p_1^2 \alpha_{o,2} + p_2^2 \alpha_{c,1}}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6} - \frac{3}{2} \frac{\alpha_{o,1} \alpha_{o,2}}{(4\pi\kappa\epsilon_0)^2} \left( \frac{I_1 I_2}{I_1 + I_2} \right) \frac{1}{z^6} \\
 &= -\frac{C_{Keesom}}{z^6} - \frac{C_{Debye}}{z^6} - \frac{C_{London}}{z^6} \\
 &= -\frac{C_{vdW}}{z^6}
 \end{aligned}$$

# What it means



# Simple Molecules

Substance	$\chi, \text{m}^3 \times 10^{18}$	$d, \text{D}$	$I, \text{eV}$	$C_{\text{Keesom}} \times 10^{79} \text{J} \cdot \text{m}^6$	$C_{\text{Debye}} \times 10^{79} \text{J} \cdot \text{m}^6$	$C_{\text{London}} \times 10^{79} \text{J} \cdot \text{m}^6$
H	0.667	0	13.6	0	0	6.3
O <sub>2</sub>	1.57	0	13.6	0	0	41.3
N <sub>2</sub>	1.74	0	15.8	0	0	59.3
Ar	1.6	0	15.8	0	0	48
He	0.2	0	24.7	0	0	1.2
CO	1.99	0.12	14.3	0.0034	0.057	67.5
HCl	2.63	1.03	13.7	18.6	5.4	105
H <sub>2</sub> O	1.48	1.84	18.0	197	10	48.8
NH <sub>3</sub>	2.24	1.5	11.7	87	10	72.6

**Table 1. Magnitudes of polarizability, dipole moment, ionization potential and energies of different weak interactions between various atoms and molecules.**

Source: <http://www.ntmdt.com/spm-basics/view/intermolecular-vdv-force>

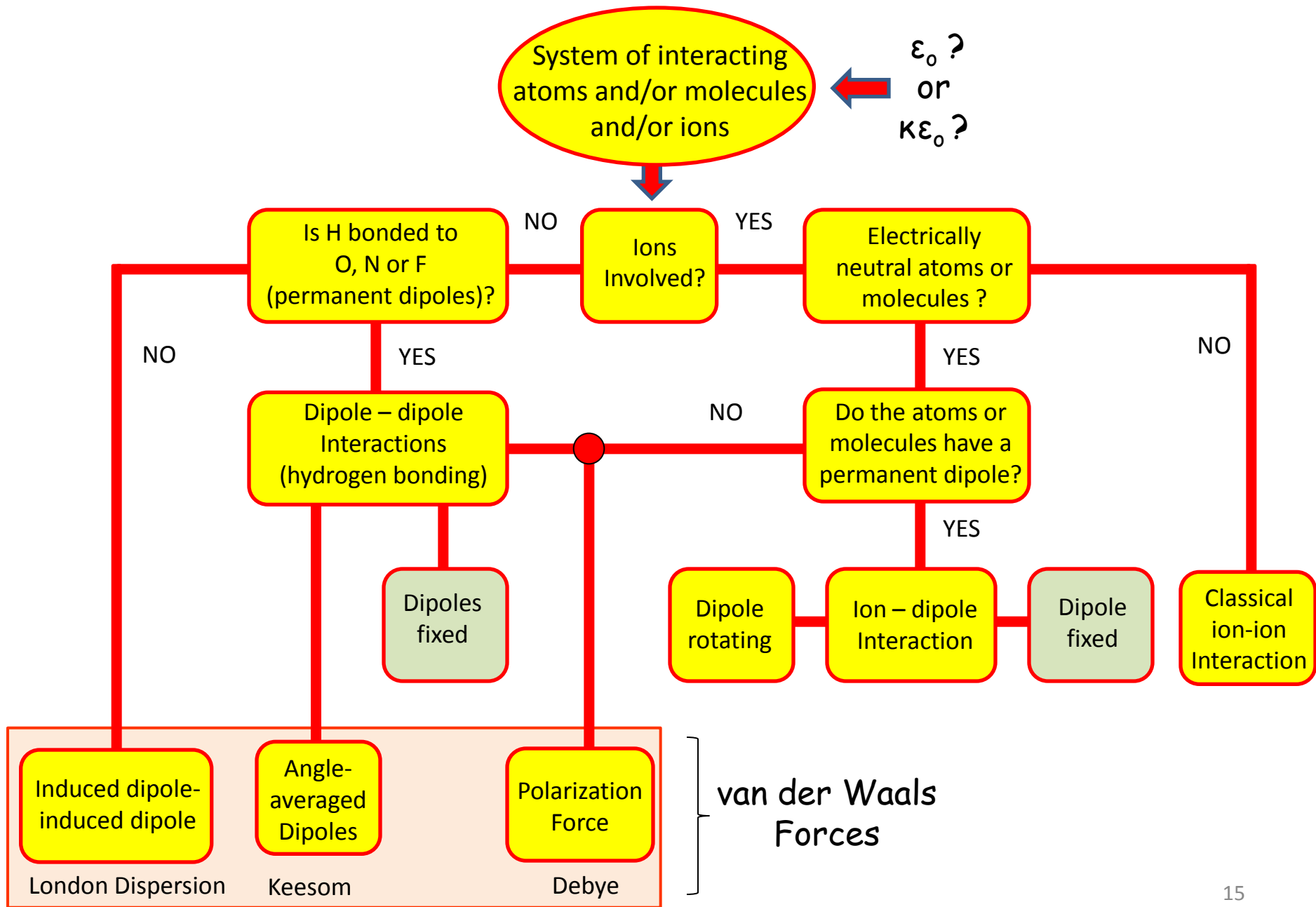
# Comparing theory and experiment

**Table 6.1:** Contributions of the Keesom, Debye, and London potential energy to the total van der Waals interaction between similar molecules as calculated with Eqs. (6.6), (6.8), and (6.9) using  $C_{total} = C_{orient} + C_{ind} + C_{disp}$ . They are given in units of  $10^{-79} \text{ Jm}^6$ . For comparison, the van der Waals coefficient  $C_{exp}$  as derived from the van der Waals equation of state for a gas  $(P + a/V_m^2) \cdot (V_m - b) = RT$  is tabulated. From the experimentally determined constants  $a$  and  $b$  the van der Waals coefficient can be calculated with  $C_{exp} = 9ab / (4\pi^2 N_A^3)$  [109] assuming that at very short range the molecules behave like hard core particles. Dipole moments  $\mu$ , polarizabilities  $\alpha$ , and the ionization energies  $h\nu$  of isolated molecules are also listed.

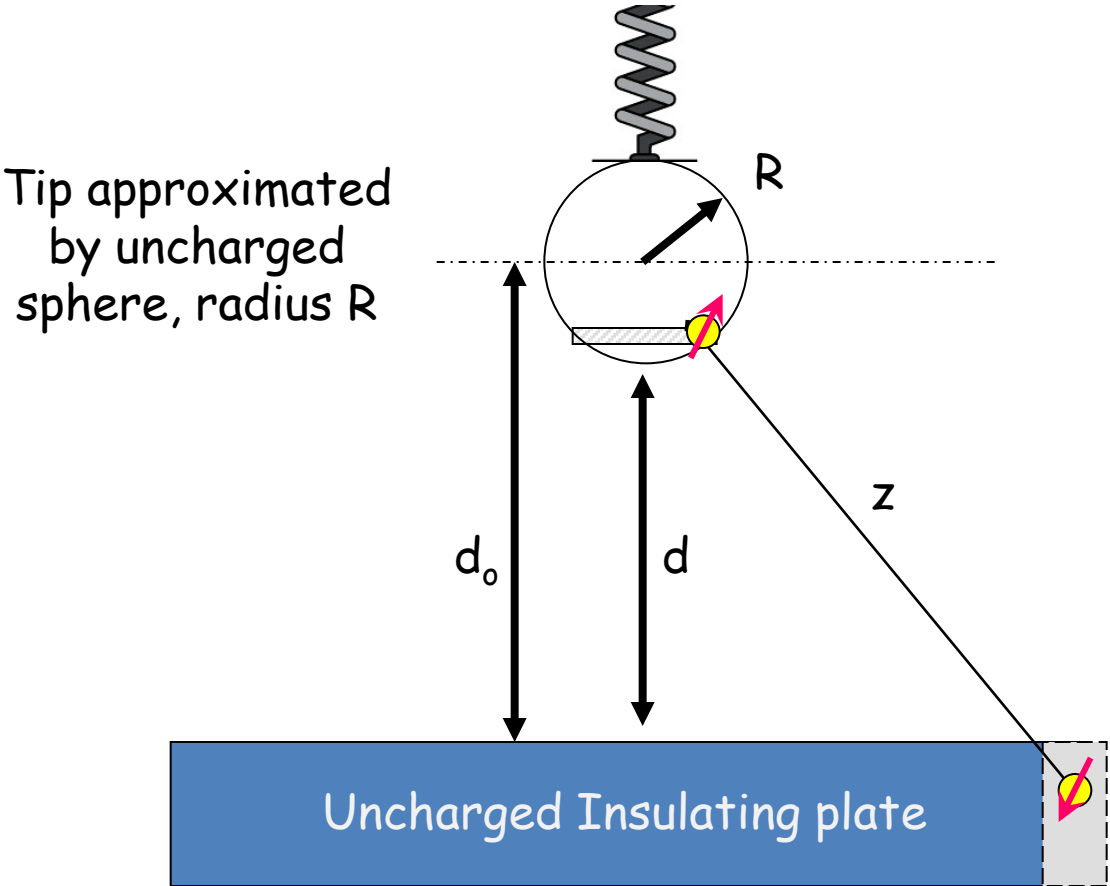
	$\mu$ (D)	$\alpha/4\pi\epsilon_0$ ( $10^{-30} \text{ m}^3$ )	$h\nu$ (eV)	$C_{orient}$	$C_{ind}$	$C_{disp}$	$C_{total}$	$C_{exp}$
He	0	0.2	24.6	0	0	1.2	1.2	0.86
Ne	0	0.40	21.6	0	0	4.1	4.1	3.6
Ar	0	1.64	15.8	0	0	50.9	50.9	45.3
CH <sub>4</sub>	0	2.59	12.5	0	0	101.1	101.1	103.3
HCl	1.04	2.7	12.8	9.5	5.8	111.7	127.0	156.8
HBr	0.79	3.61	11.7	3.2	4.5	182.6	190.2	207.4
HI	0.45	5.4	10.4	0.3	2.2	364.0	366.5	349.2
CHCl <sub>3</sub>	1.04	8.8	11.4	9.5	19.0	1058	1086	1632
CH <sub>3</sub> OH	1.69	3.2	10.9	66.2	18.3	133.5	217.9	651.0
NH <sub>3</sub>	1.46	2.3	10.2	36.9	9.8	64.6	111.2	163.7
H <sub>2</sub> O	1.85	1.46	12.6	95.8	10.0	32.3	138.2	176.2
CO	0.11	1.95	14.0	0.0012	0.047	64.0	64.1	60.7
CO <sub>2</sub>	0	2.91	13.8	0	0	140.1	140.1	163.6
N <sub>2</sub>	0	1.74	15.6	0	0	56.7	56.7	55.3
O <sub>2</sub>	0	1.58	12.1	0	0	36.2	36.2	46.0

Source: *Physics and Chemistry of Interfaces*, H.-J. Butt, K. Graf, M. Kappl, Wiley-VCH (2003).

# Summary of Coulombic Intermolecular Forces



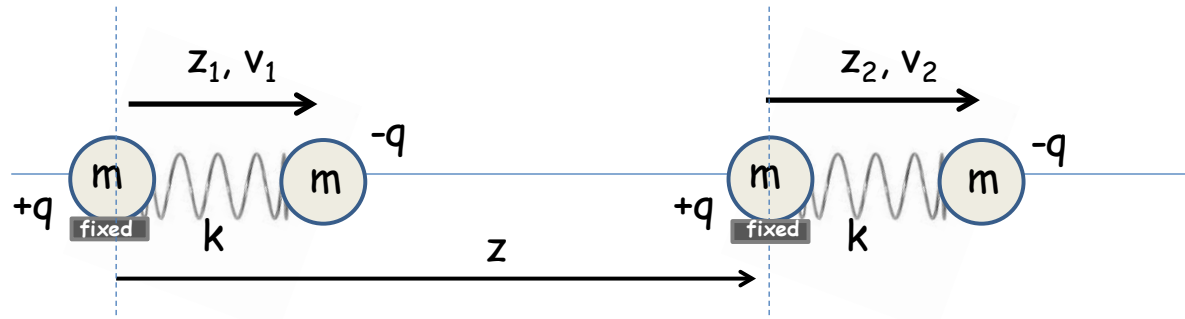
# Next up, the interaction between a tip and a substrate





# Appendix A: Dispersion Forces - a simple model

Consider the diagram below which shows two small masses vibrating in a parabolic well that is modeled by an effective spring with spring constant  $k$ . The two fixed (non-vibrating) atoms are separated by a distance  $z$  as shown.



As indicated, the instantaneous displacement of the moveable mass  $m$  from equilibrium is specified by  $z_1$  and  $z_2$ , respectively. Assume for the moment that the masses have zero charge. Schrödinger's equation for the two uncoupled oscillators requires a specification of the interaction potential energy  $U$  for each oscillator. For a parabolic well,  $U$  is specified as

$$U_1(z) = \frac{1}{2}kz_1^2 = m\omega_o^2 z_1^2 \quad \text{and} \quad U_2(z) = \frac{1}{2}kz_2^2 = m\omega_o^2 z_2^2.$$

Because  $U$  is uncoupled, Schrödinger's equation reduces to two separate equations with solutions that are given in many quantum textbooks:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_1^2} \right] \Psi + \frac{1}{2}m\omega_o^2 z_1^2 \Psi = E_1 \Psi$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_2^2} \right] \Psi + \frac{1}{2}m\omega_o^2 z_2^2 \Psi = E_2 \Psi$$

The known solutions of these two equations tells us that the quantum mechanical eigenvalues  $E_1$  and  $E_2$  for the oscillator are quantized, with the lowest energy solution (the ground state energy) given by

$$E_{tot} = E_1 + E_2 = \frac{1}{2}(\hbar\omega_o + \hbar\omega_o) = \hbar\omega_o$$

where  $\hbar$  is Planck's constant divided by  $2\pi$  and  $\omega_o = \sqrt{\frac{k}{m}}$ .

If each spring system acquires a charge  $\pm q$  as shown in the diagram above, then each spring will acquire an instantaneous, fluctuating dipole moment  $p_1=qz_1$  and  $p_2=qz_2$ . What is the resulting electrostatic potential energy  $U_{electr}$  that results when these two dipoles interact? The answer can be written down by inspection:

$$U_{electr}(z) = \frac{1}{4\pi\epsilon_o} \left[ \frac{q^2}{z} - \frac{q^2}{z+z_2} - \frac{q^2}{z-z_1} + \frac{q^2}{(z-z_1)+z_2} \right]$$

If  $z \gg z_1$  and  $z \gg z_2$ , you can derive a simple expression for  $U_{electr}$  by using the binomial expansion as follows:

$$\begin{aligned}
U_{electr} &= \frac{1}{4\pi\epsilon_0} \left[ \frac{q^2}{z} - \frac{q^2}{z+z_2} - \frac{q^2}{z-z_1} + \frac{q^2}{(z-z_1)+z_2} \right] \\
&= \frac{1}{4\pi\epsilon_0} \frac{q^2}{z} \left[ 1 - \frac{1}{1+\frac{z_2}{z}} - \frac{1}{1-\frac{z_1}{z}} + \frac{1}{1+\frac{z_2-z_1}{z}} \right] \\
&= \frac{1}{4\pi\epsilon_0} \frac{q^2}{z} \left[ 1 - \left(1 + \frac{z_2}{z}\right)^{-1} - \left(1 - \frac{z_1}{z}\right)^{-1} + \left(1 + \frac{z_2-z_1}{z}\right)^{-1} \right]
\end{aligned}$$

$$(1+\epsilon)^n \simeq 1+n\epsilon + \frac{n(n-1)}{2!}\epsilon^2 + \dots \quad (1+(-\epsilon))^n \simeq 1-n\epsilon + \frac{n(n-1)}{2!}\epsilon^2 + \dots$$

we have :

$$\left(1 + \frac{z_2}{z}\right)^{-1} \simeq 1 - \frac{z_2}{z} + \left(\frac{z_2}{z}\right)^2 + \dots \quad \left(1 - \frac{z_1}{z}\right)^{-1} \simeq 1 + \frac{z_1}{z} + \left(\frac{z_1}{z}\right)^2 + \dots$$

$$\left(1 + \frac{z_2-z_1}{z}\right)^{-1} \simeq 1 - \frac{z_2-z_1}{z} + \left(\frac{z_2-z_1}{z}\right)^2 + \dots$$

$$\begin{aligned}
U_{electr} &= \frac{1}{4\pi\epsilon_0} \frac{q^2}{z} \left[ 1 - \left(1 - \frac{z_2}{z} + \frac{\left(z_2^2\right)}{z^2} + \dots\right) - \left(1 + \frac{z_1}{z} + \frac{\left(z_1^2\right)}{z^2} + \dots\right) + \left(1 - \frac{z_2-z_1}{z} + \frac{\left(z_2^2 - 2z_2z_1 + z_1^2\right)}{z^2} + \dots\right) \right] \\
&\simeq \frac{1}{4\pi\epsilon_0} \frac{q^2}{z} \left[ 1 - 1 + \frac{z_2}{z} - \frac{\left(z_2^2\right)}{z^2} - 1 - \frac{z_1}{z} - \frac{\left(z_1^2\right)}{z^2} + 1 - \frac{z_2}{z} + \frac{z_1}{z} + \frac{z_2^2}{z^2} - \frac{2z_2z_1}{z^2} + \frac{z_1^2}{z^2} \right] \\
&= \frac{1}{4\pi\epsilon_0} \frac{q^2}{z} \left[ -\frac{2z_2z_1}{z^2} \right] = -\frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} z_2z_1
\end{aligned}$$

This gives a new expression for the total potential energy of the system,  $U_{tot}$ :

$$U_{tot} = U_1 + U_2 + U_{elect} = \frac{1}{2}kz_1^2 + \frac{1}{2}kz_2^2 - \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} z_2 z_1$$

When this expression is used in Schrödinger's equation, the solutions are not so simple because the electrostatic potential energy term now contains **both**  $z_1$  and  $z_2$ . Not surprisingly, the vibrational frequencies for each spring will be altered because of this electrostatic interaction. The question is by how much will they change?

The cross-term in the expression for  $U_{tot}$  prevents a simple answer to this question. However, if we could somehow rewrite the expression for  $U_{tot}$  to have a separable form, something like

$$U_{tot} = \frac{1}{2}k_s (z_1 + z_2)^2 + \frac{1}{2}k_a (z_1 - z_2)^2$$

then we could define new coordinate variables  $z_s = (z_1 + z_2)/\sqrt{2}$  and  $z_a = (z_1 - z_2)/\sqrt{2}$ , with  $k_s$  and  $k_a$  defined as some "equivalent" spring constants. Schrödinger's equation could then be rewritten in the same form as the uncoupled case above:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_s^2} \right] \Psi + \frac{1}{2} m \omega_s^2 z_s^2 \Psi = E_s \Psi$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_a^2} \right] \Psi + \frac{1}{2} m \omega_a^2 z_a^2 \Psi = E_a \Psi$$

This can be accomplished by setting

$$\frac{1}{2}kz_1^2 + \frac{1}{2}kz_2^2 - \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} z_2 z_1 = \frac{1}{2}k_s \frac{(z_1 + z_2)^2}{2} + \frac{1}{2}k_a \frac{(z_1 - z_2)^2}{2},$$

The algebra is given below:

$$\text{Let } \frac{1}{2}kz_1^2 + \frac{1}{2}kz_2^2 - \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} z_2 z_1 = \frac{1}{2}k_s \frac{(z_1 + z_2)^2}{2} + \frac{1}{2}k_a \frac{(z_1 - z_2)^2}{2}$$

$$k(z_1^2 + z_2^2) - \frac{1}{\pi\epsilon_0} \frac{q^2}{z^3} z_2 z_1 = \frac{1}{2}(k_s + k_a)(z_1^2 + z_2^2) + z_1 z_2 (k_s - k_a)$$

$$\text{evidently, } 2k = k_s + k_a \quad \text{and} \quad -\frac{1}{\pi\epsilon_0} \frac{q^2}{z^3} = (k_s - k_a)$$

$$\text{substituting gives } -\frac{1}{\pi\epsilon_0} \frac{q^2}{z^3} = (2k - k_a - k_a) = 2(k - k_a)$$

$$-\frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} = k - k_a \Rightarrow k_a = \left( k + \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} \right)$$

$$k_s = 2k - k_a = 2k - \left( k + \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} \right) = \left( k - \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3} \right)$$

It follows that for the electrostatically coupled system, the new eigenfrequencies are now given by

$$\omega_s = \sqrt{\frac{k - \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3}}{m}} \quad \text{and} \quad \omega_a = \sqrt{\frac{k + \frac{1}{2\pi\epsilon_0} \frac{q^2}{z^3}}{m}}$$

What is the change in the quantum ground state energy,  $\Delta U$ , from the uncoupled case and how does it vary with  $z$ ? Define  $\Delta U$  by

$$\Delta U = \frac{1}{2}(\hbar\omega_a + \hbar\omega_s) - 2 \times \frac{1}{2}\hbar\omega_0$$

If  $\Delta U$  is a positive number, the coupled system will have a higher potential energy and the two charged springs will experience a repulsive force. If  $\Delta U$  is a negative number, the coupled system will have a lower potential energy and the two charged springs will experience an attractive force.

The details of the calculation for  $\Delta U$  are provided on the next page. The result is

$$\Delta U(z) = -\frac{1}{2}\hbar\omega_0 \left( \left( \frac{1}{4\pi\epsilon_0} \frac{q^2}{k} \right)^2 \right) \frac{1}{z^6}$$

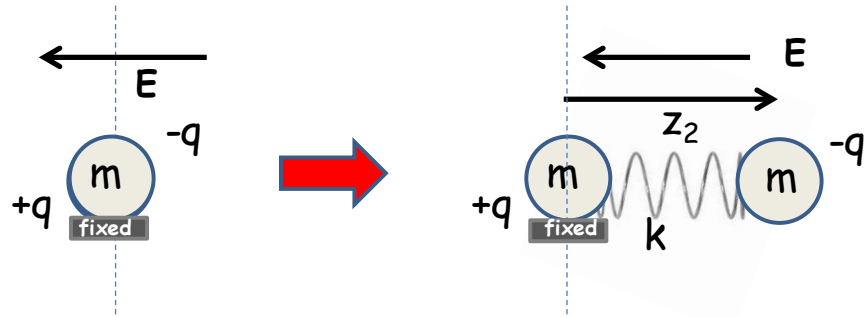
Since  $\Delta U$  is a negative number, the coupled system will have a lower potential energy and the two springs will experience an attractive potential that varies as  $z^{-6}$ .

$$\begin{aligned}
\Delta U &= \frac{1}{2} [(\hbar\omega_a + \hbar\omega_s) - 2\hbar\omega_o] = \frac{1}{2}(\hbar\omega_a + \hbar\omega_s) - \hbar\omega_o \\
&= \frac{\hbar}{2} \left( \sqrt{\frac{k + \frac{1}{2\pi\epsilon_o} \frac{q^2}{z^3}}{m}} + \sqrt{\frac{k - \frac{1}{2\pi\epsilon_o} \frac{q^2}{z^3}}{m}} \right) - \hbar\sqrt{\frac{k}{m}} = \frac{\hbar}{2} \left( \sqrt{\frac{k}{m}} \sqrt{1 + \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} + \sqrt{\frac{k}{m}} \sqrt{1 - \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} \right) - \hbar\sqrt{\frac{k}{m}} \\
&= \frac{\hbar}{2} \left( \sqrt{\frac{k}{m}} \left( \sqrt{1 + \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} \right)^{\frac{1}{2}} + \sqrt{\frac{k}{m}} \left( \sqrt{1 - \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} \right)^{\frac{1}{2}} \right) - \hbar\sqrt{\frac{k}{m}} \\
&= \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left( \left( \sqrt{1 + \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} \right)^{\frac{1}{2}} + \left( \sqrt{1 - \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3}} \right)^{\frac{1}{2}} - 2 \right)
\end{aligned}$$

expanding using  $(a + \epsilon)^n \approx a^n + na^{n-1}\epsilon + \frac{n(n-1)}{2!}a^{n-2}\epsilon^2 + \dots$

$$\begin{aligned}
&\approx \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left( 1 + \frac{1}{2} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right) + \frac{1}{2} \cdot \frac{1}{2} \cdot \left( \frac{1}{2} - 1 \right) \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 + \dots \right. \\
&\quad \left. + 1 + \frac{1}{2} \left( -\frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right) + \frac{1}{2} \cdot \frac{1}{2} \cdot \left( \frac{1}{2} - 1 \right) \left( -\frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 + \dots - 2 \right) \\
&= \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left( 1 + \frac{1}{2} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right) - \frac{1}{8} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 + \dots + 1 - \frac{1}{2} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right) - \frac{1}{8} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 + \dots - 2 \right) \\
&= \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left( -\frac{1}{4} \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 \right) \\
&= -\frac{1}{8} \hbar\omega_o \left( \left( \frac{1}{2\pi\epsilon_o} \frac{1}{k} \frac{q^2}{z^3} \right)^2 \right) = -\frac{1}{2} \hbar\omega_o \left( \left( \frac{1}{4\pi\epsilon_o} \frac{q^2}{k} \right)^2 \right) \frac{1}{z^6}
\end{aligned}$$

Note that the final answer contains  $q$  and  $k$ , parameters that are easy to define but difficult to know. These two parameters can be eliminated by realizing that an electric field **causes** the charge separation by exerting a force which must be balanced by the "effective" spring that tethers the separated charges together. The spring will "stretch" until the restoring force of the spring matches the electrostatic force produced by the electric field.



In equilibrium, this implies that

$$|q|E = kz_2$$

In equilibrium, the electric field will induce a dipole moment  $p_{ind} = qz_2 = \alpha E$ . This gives

$$p_{ind} \equiv |q|z_2 = q \left( \frac{q}{k} E \right) = \alpha E$$

$$\text{evidently } \frac{q^2}{k} = \alpha$$



This finally allows us to write

$$\Delta U(z) = -\frac{1}{2} \hbar \omega_o \left( \left( \frac{1}{4\pi\epsilon_o} \frac{q^2}{k} \right)^2 \right) \frac{1}{z^6} = -\frac{1}{2} \hbar \omega_o \left( \left( \frac{\alpha}{4\pi\epsilon_o} \right)^2 \right) \frac{1}{z^6} = -\frac{1}{2} \frac{\alpha^2 \hbar \omega_o}{(4\pi\epsilon_o)^2} \frac{1}{z^6}$$

The parameter  $\hbar \omega_o$  represents a characteristic "motional" frequency of the charge in a polarized atom/molecule and is often replaced by the ionization energy  $I$ , which is a well known and easy-to-measure quantity. This gives rise to the result often quoted in the literature

$$\Delta U(z) = -\frac{1}{2} \frac{\alpha^2 I}{(4\pi\epsilon_o)^2} \frac{1}{z^6}$$

The equivalent result in 3-dimensions is

$$\Delta U(z) = -\frac{3}{4} \frac{\alpha^2 I}{(4\pi\epsilon_o)^2} \frac{1}{z^6}$$