

The Dispersion energy

An introduction and some Surprises

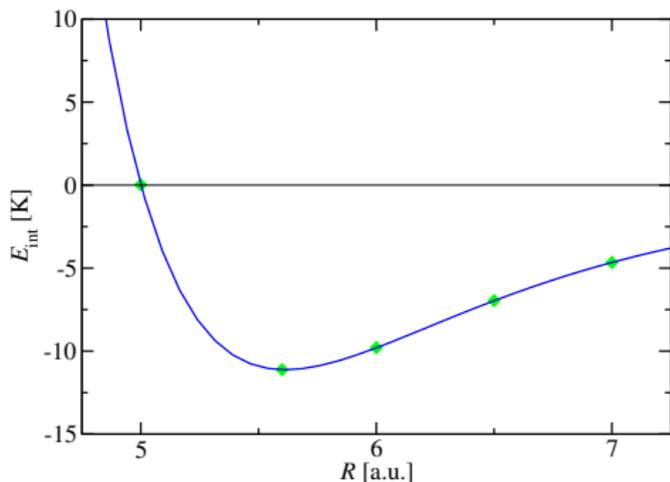
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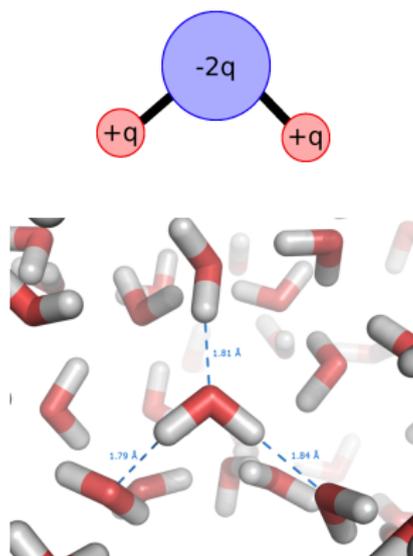
Sometime in August 2009, in a Splendid place in Italy

Molecular Interactions

- ▶ Gases condense, so there must be an attractive force between the molecules at long range.
- ▶ Liquids have finite volume and low compressibility, so there must be a steep repulsive region at shorter distances.

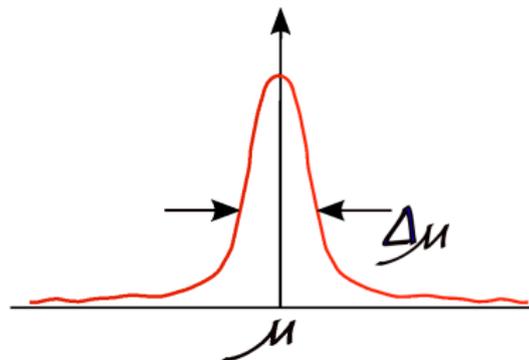


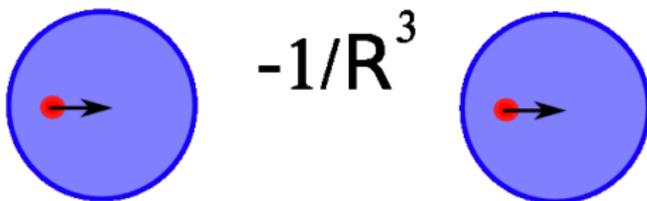
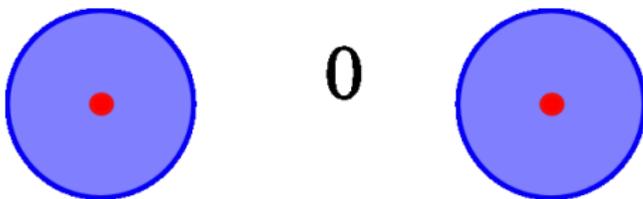
- ▶ *Attraction*: Electrostatic, polarization (second-order electrostatic interaction).
- ▶ *Repulsion*: Pauli repulsion (Coulomb repulsion is also possible).



What about Helium?

- ▶ Liquid Helium exists so there must be an attraction between helium atoms.
- ▶ But helium atoms are spherical. So the attraction cannot arise from a classical electrostatic interaction.
- ▶ *Q: How do we know that helium atoms are spherical?*
- ▶ *A: Measure the dipole moment.*



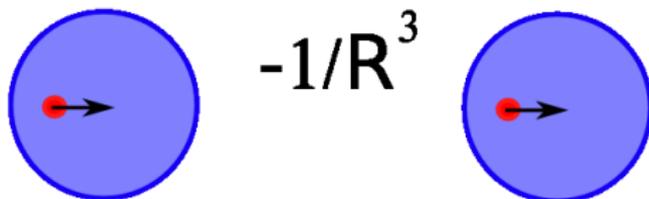
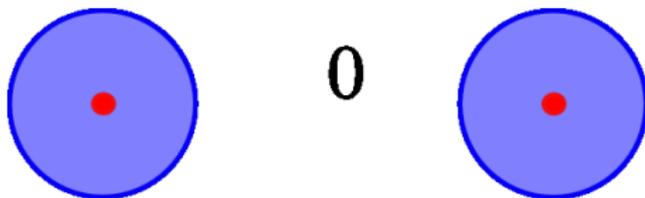


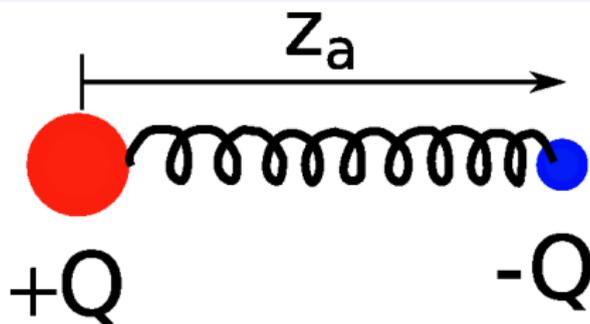
Recall: Mean force of attraction between two dipoles in thermal equilibrium is $\langle F \rangle \sim -\frac{1}{kT} \frac{1}{R^7}$.

Picture so far:

- ▶ Present even at 0° K. So cannot be due to thermal fluctuations.
- ▶ Purely quantum phenomenon.
- ▶ Always attractive (we have not shown this).
- ▶ Semi-classical interpretation: correlations in spontaneous fluctuations.

Drude model for the Dispersion

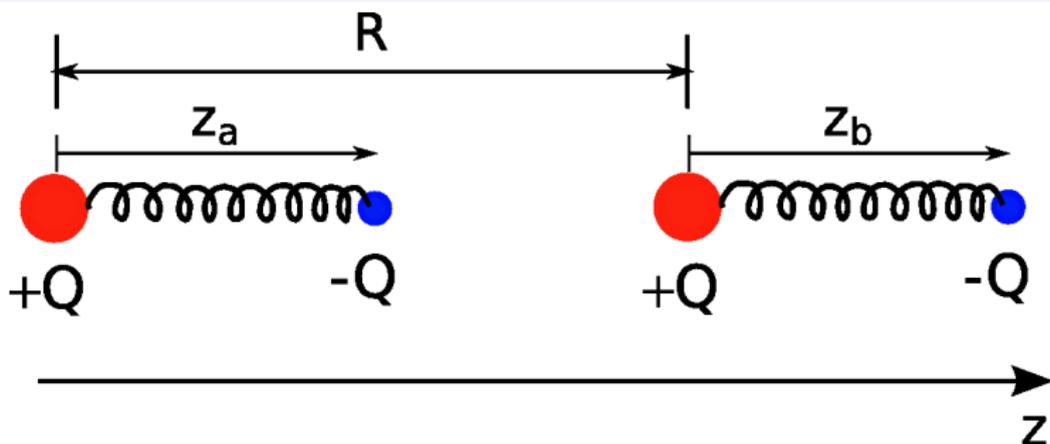




$$H_a \psi = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dz_a^2} + \frac{1}{2} k z_a^2 \right) \psi = E_a \psi \quad (1)$$

$$\mu_a = Q z_a \quad (2)$$

$$E_a = \left(n_a + \frac{1}{2} \right) \hbar \omega \quad (3)$$



- ▶ $R \rightarrow \infty$: Two independent oscillators:
 $E(\infty) = E_a + E_b = (n_a + n_b + 1)\hbar\omega$.
- ▶ Finite R : Interacting oscillators with potential:

$$V = -\frac{2Q^2}{4\pi\epsilon_0 R^3} z_a z_b = -C z_a z_b. \quad (4)$$

Dimer Hamiltonian:

$$\begin{aligned} H &= H_a + H_b + V \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dz_a^2} + \frac{1}{2}kz_a^2 - \frac{\hbar^2}{2m} \frac{d^2}{dz_b^2} + \frac{1}{2}kz_b^2 - cz_a z_b \end{aligned} \quad (5)$$

Can be very easily solved by changing coordinates to $Z_1 = (z_a + z_b)/2$ and $Z_2 = (z_a - z_b)/2$. In these coordinates we get

$$H = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dZ_1^2} + \frac{d^2}{dZ_2^2} \right) + \frac{1}{2}k_1 Z_1^2 + \frac{1}{2}k_2 Z_2^2. \quad (6)$$

where

$$k_1 = k + c = k + \frac{2Q^2}{4\pi\epsilon_0 R^3}, \quad (7)$$

and, $k_2 = k - c$.

Therefore, the energy at finite R is

$$\begin{aligned} E(R) &= E_1 + E_2 \\ &= \left(n_1 + \frac{1}{2}\right)\hbar\omega_1 + \left(n_2 + \frac{1}{2}\right)\hbar\omega_2, \end{aligned} \quad (8)$$

where

$$\begin{aligned} \omega_1 &= \sqrt{\frac{k_1}{m}} = \sqrt{\frac{k+c}{m}} \\ &= \sqrt{\frac{k}{m}} \left(1 + \frac{1}{2} \left(\frac{c}{k}\right) - \frac{1}{8} \left(\frac{c}{k}\right)^2 + \dots\right) \end{aligned} \quad (9)$$

The expansion is valid if R is large enough.

We now have all of it. Let's calculate the energy of the ground state.

$$\begin{aligned} E_0(R) &= \frac{1}{2} \hbar(\omega_1 + \omega_2) \\ &= \hbar\omega - \frac{\hbar\omega Q^4}{2(4\pi\epsilon_0)^2 k^2 R^6} - \dots \\ &= E_0(\infty) - \frac{C_6}{R^6} - \dots \end{aligned} \tag{10}$$

So the system is stabilized by the correlation term. The stabilization energy is the dispersion.

Let's re-write C_6 in terms of more recognisable quantities:

- ▶ **Force balance** $kz = QE$ so $z = \frac{QE}{k}$.
- ▶ **Dipole moment** $\mu = zQ = \frac{Q^2E}{k}$.
- ▶ **Polarizability** $\mu = \alpha E$ therefore $\alpha = \frac{Q^2}{k}$.
- ▶ **Excitation energy** London suggested we use $\hbar\omega = E_I$, the vertical ionization energy.

So we get (including a 3-D factor),

$$C_6 = \frac{3\alpha^2 E_I}{4(4\pi\epsilon_0)^2}. \quad (11)$$

The Hellmann–Feynmann force theorem

Recap of the theorem:

- ▶ $H(\lambda)$ is an Hermitian operator that depends on a parameter λ .
- ▶ $H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$ s.t. $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$.
- ▶ $E(\lambda) = \langle\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle$.
- ▶ H–F theorem:

$$\frac{dE(\lambda)}{d\lambda} = \langle\psi(\lambda)|\frac{dH(\lambda)}{d\lambda}|\psi(\lambda)\rangle. \quad (12)$$

- ▶ Also holds for approximate solutions as long as they are variational. (Prove it!)

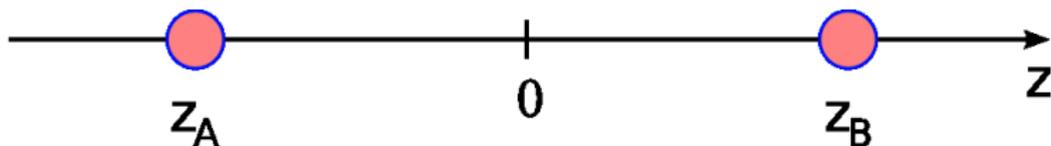
Now consider the helium dimer (Born–Oppenheimer approximation) separated by distance R :

$$H = -\frac{1}{2}\nabla_1^2 - \frac{2}{|\mathbf{r}_1 - \mathcal{R}_A|} - \frac{1}{2}\nabla_2^2 - \frac{2}{|\mathbf{r}_2 - \mathcal{R}_B|} \\ - \frac{2}{|\mathbf{r}_1 - \mathcal{R}_B|} - \frac{2}{|\mathbf{r}_2 - \mathcal{R}_A|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{4}{|\mathcal{R}_A - \mathcal{R}_B|}$$

Place the two atoms along the z -axis. And take $\lambda = Z_A$. So we can use the H–F theorem to calculate the force on nucleus A :

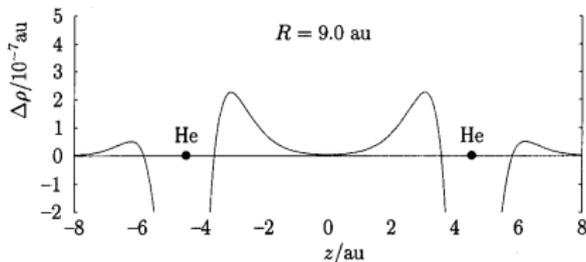
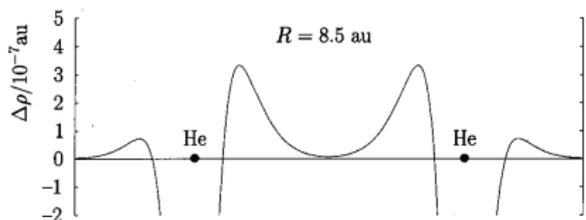
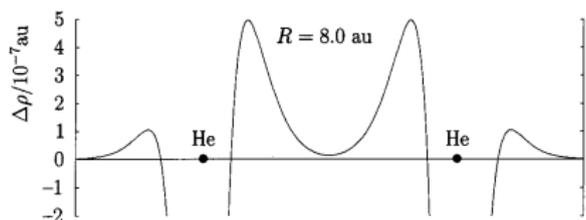
$$-F_A = \frac{dE}{dZ_A} = \langle \psi | \frac{dH}{dZ_A} | \psi \rangle \\ = +\frac{4}{R^2} - 2 \int \frac{\rho(\mathbf{r})}{|\mathcal{R}_A - \mathbf{r}|^3} (Z_A - z) d\mathbf{r} \quad (13)$$

$$F_A = -\frac{4}{R^2} + 2 \int \frac{\rho(\mathbf{r})}{|\mathcal{R}_A - \mathbf{r}|^3} (Z_A - z) d\mathbf{r}$$



- ▶ The first term is repulsive. So the attraction must come from the second term alone.
- ▶ Write $\rho = (\rho_A^0 + \rho_B^0) + \Delta\rho$, where ρ_A^0 and ρ_B^0 are the un-distorted, spherically symmetric densities for the helium atoms.
- ▶ The attraction must arise from $\Delta\rho$ alone.

Allen & Tozer (2002)
calculated $\Delta\rho$ using
the BD(T) method
(Breuckner Doubles
with non-iterated triple
excitations).



Feynmann (1939):

The Schrödinger perturbation theory for two interacting atoms at a separation R , ..., leads to the result that the charge distribution of each is distorted from central symmetry, a dipole moment of order $1/R^7$ being induced in each atom. The negative charge distribution of each atom has its center of gravity moved towards the other.

Concepts: Polarizability

$$U = -\mu E - \frac{1}{2}\alpha E^2 - \frac{\beta}{6}E^3 - \dots$$

The polarizability, α , can be defined as $\alpha = -\partial^2 U / \partial E^2|_{E=0}$. Or, using an expression from perturbation theory:

$$\begin{aligned} \alpha &= \sum'_n \frac{\langle 0|x|n\rangle \langle n|x|0\rangle}{E_n - E_0} \\ &= \iint x \alpha(\mathbf{r}, \mathbf{r}'; 0) x' d\mathbf{r} d\mathbf{r}' \end{aligned}$$

Multipole expansion:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{R} - \frac{1}{R^5}(2z_1 z_2 - x_1 x_2 - y_1 y_2) + \dots$$

Dispersion

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty du \int \frac{\alpha_A(\mathbf{r}_1, \mathbf{r}'_1; iu) \alpha_B(\mathbf{r}_2, \mathbf{r}'_2; iu)}{|\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}'_1 - \mathbf{r}'_2|} d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2$$

For two atoms, using the multipole expansion and the definition of the polarizabilities, this becomes

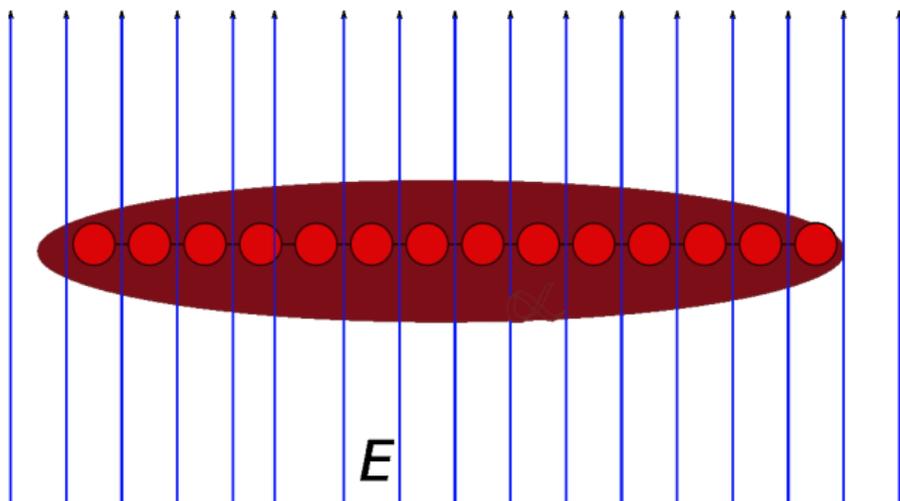
$$E_{\text{disp}}^{(2)} = -\frac{3}{\pi R^6} \int_0^\infty \alpha_A(iu) \alpha_B(iu) du - \dots$$

Q: Why no charge term from the multipole expansion?

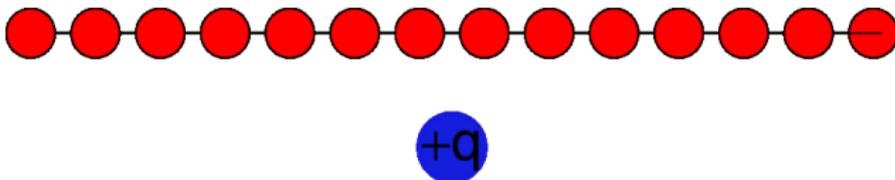
A: Charge conservation means such terms are all zero.

$$\begin{aligned} E_{\text{disp}}^{(2)} &= -\frac{1}{\pi} \sum_a \sum_b T_{tu}^{ab} T_{t'u'}^{ab} \int_0^\infty \alpha_{tt'}^a(iw) \alpha_{uu'}^b(iw) dw \\ &= -\sum_a \sum_b \left(\frac{C_6^{ab}}{R_{ab}^6} + \frac{C_7^{ab}}{R_{ab}^7} + \frac{C_8^{ab}}{R_{ab}^8} + \dots \right) \end{aligned}$$

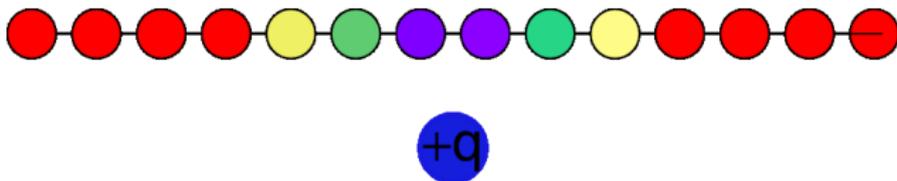
Distribution When does the molecular polarizability make physical sense?



More likely, the molecule is in a non-uniform field. Does the total molecular polarizability make sense now?



Or do we need to use some sort of *local polarizability*?



- ▶ The polarizability is derived from the density-response function that is a *non-local* object: it tells us how a perturbation at some point propagates to another.
- ▶ This is reflected in the distributed polarizabilities: they depend on *pairs of sites*:

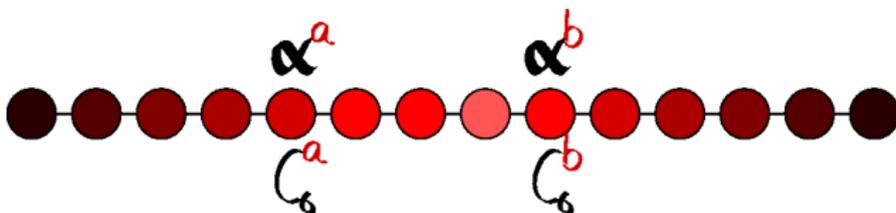
$$\alpha^{ab} \tag{14}$$

- ▶ This term describes the change in the dipole moment at site a due to the electric field at site b :

$$\Delta\mu^a = -\alpha^{ab} E^b. \quad (15)$$

- ▶ The non-local terms typically decay exponentially with distance of the sites. Viewed in matrix form we get a band-diagonal matrix.
- ▶ The non-local terms can be transformed into local terms. This is an approximation, but works rather well...
- ▶ The local polarizabilities give rise to local C_6 coefficients.
- ▶ This is the source of the concept of *$-C_6/R^6$ terms between every pair of sites in two interacting molecules.*

Here is the picture you should have in mind:

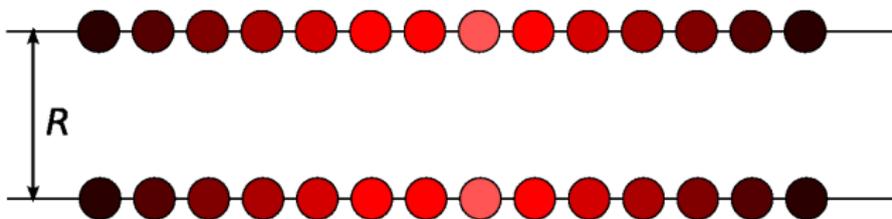


Assumption:

$$\alpha^{ab} \sim e^{-\gamma R_{ab}}$$

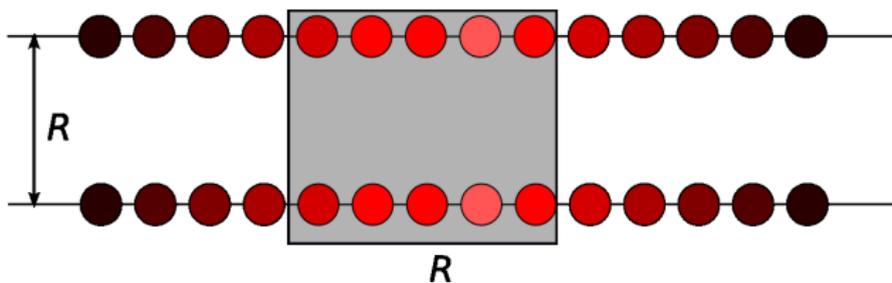
Valid for materials with a finite band/HOMO–LUMO gap

Interactions between extended objects Infinite, parallel chains with finite gap



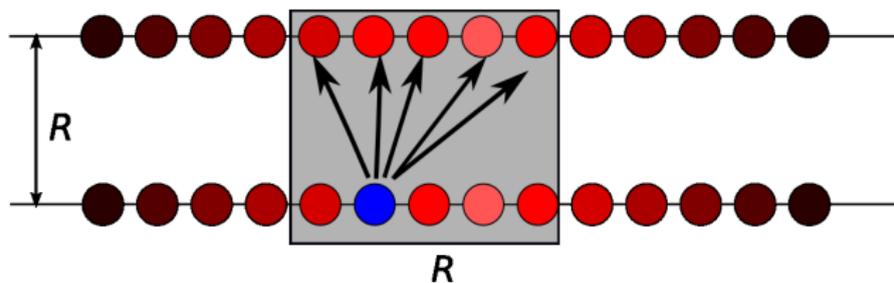
► Length scale: R

Infinite, parallel chains with finite gap



- ▶ Length scale: R
- ▶ Select section of order R .

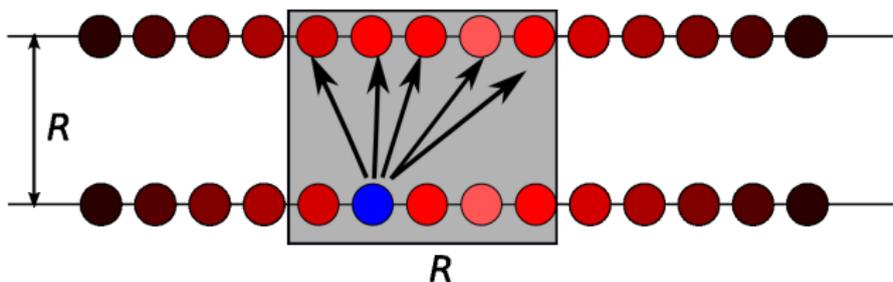
Infinite, parallel chains with finite gap



- Interaction of blue atom with others is:

$$-\frac{C_6}{R^6} \times R \quad (16)$$

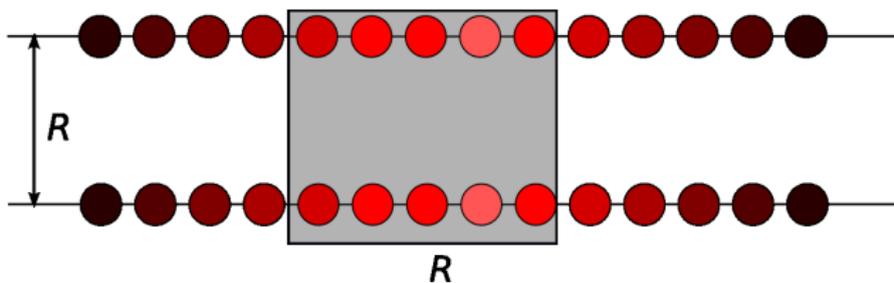
Infinite, parallel chains with finite gap



- ▶ But there are order R blue atoms, so interaction between the bits in the box is:

$$-\frac{C_6}{R^6} \times R \times R \quad (17)$$

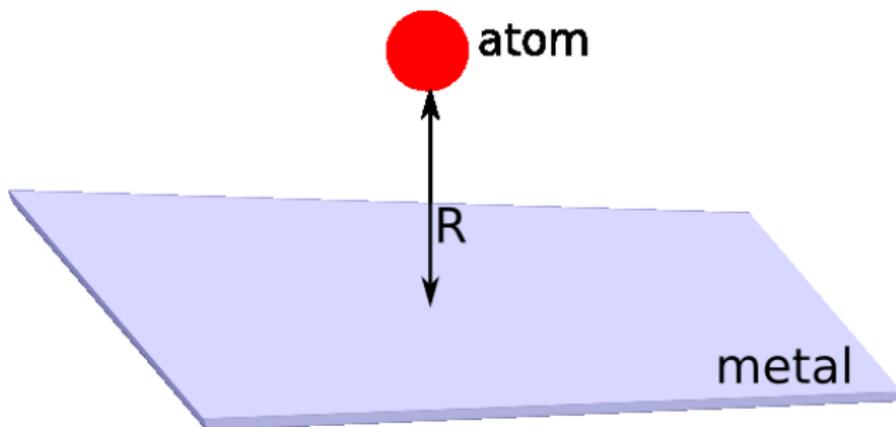
Infinite, parallel chains with finite gap



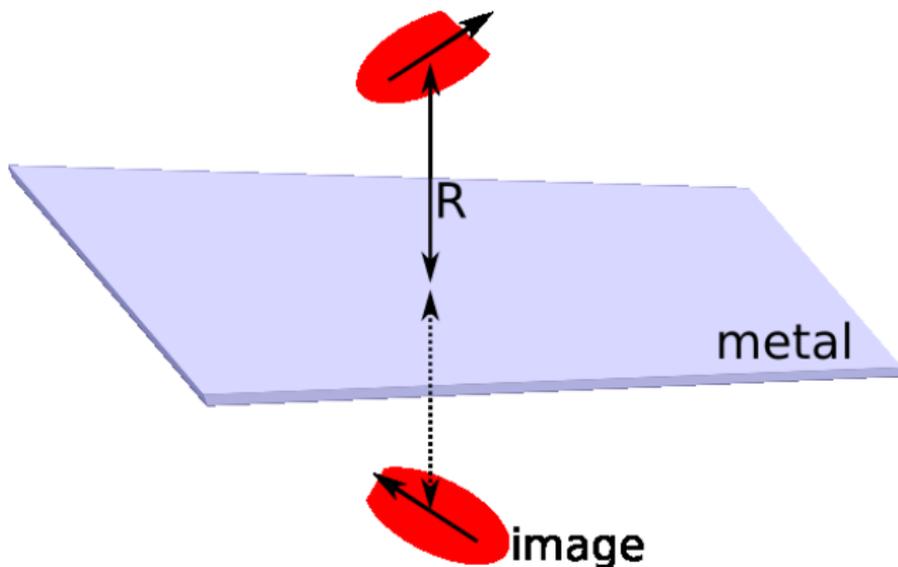
- And interaction per unit length is:

$$-\frac{C_6}{R^6} \times R \times R/R = -\frac{C_6}{R^5} \quad (18)$$

What about metals? Something must be different and a simple example of an atom interacting with a thin metallic (infinite) plane shows us this:



Any fluctuation in the atom is mirrored (oppositely) by the metallic sheet. So a dipolar fluctuation sees a *perfectly correlated image dipole*.



So the resulting interaction will be

$$\sim -\frac{C_3}{R^3}$$

But it is quite different for insulators. The same sort of analysis as we did for the interaction between infinite chains will give us:

- ▶ Atom ··· thin-sheet:

$$\sim -\frac{C}{R^4}$$

- ▶ Atom ··· thick-sheet:

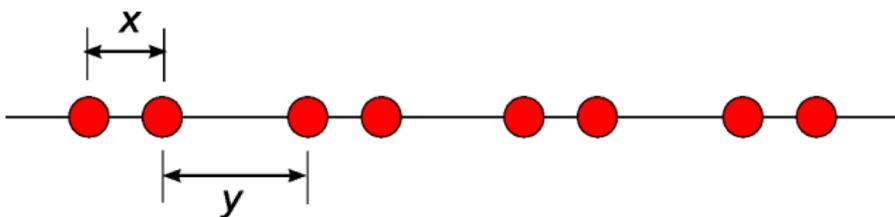
$$\sim -\frac{C}{R^3}$$

Dobson, White & Rubio, PRL **96**, (2006).

System	Metals	Insulators
1-D	$-R^{-2}(\ln(KR))^{-3/2}$	$-R^{-5}$
2-D	$-R^{-5/2}$	$-R^{-4}$

Verified using DMC calculations on the 1-D and 2-D HEG by Drummond & Needs (PRL **99**, (2007)).

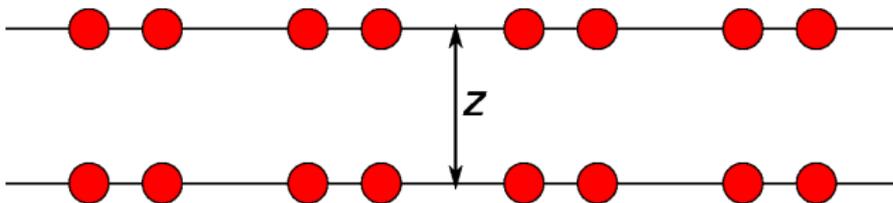
H₂ chains



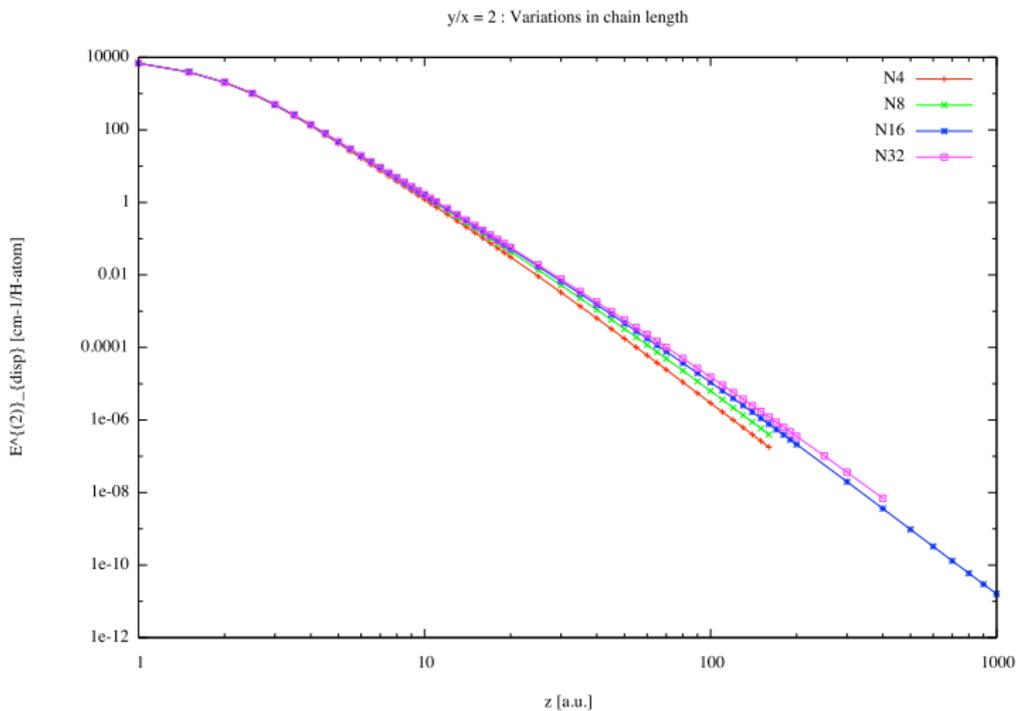
- ▶ Distortion parameter: $\xi = y/x$.
- ▶ Finite chains (64 H atoms). Ali Alavi and James Spencer have looked at infinite chains.
- ▶ Variation in HOMO–LUMO gap.

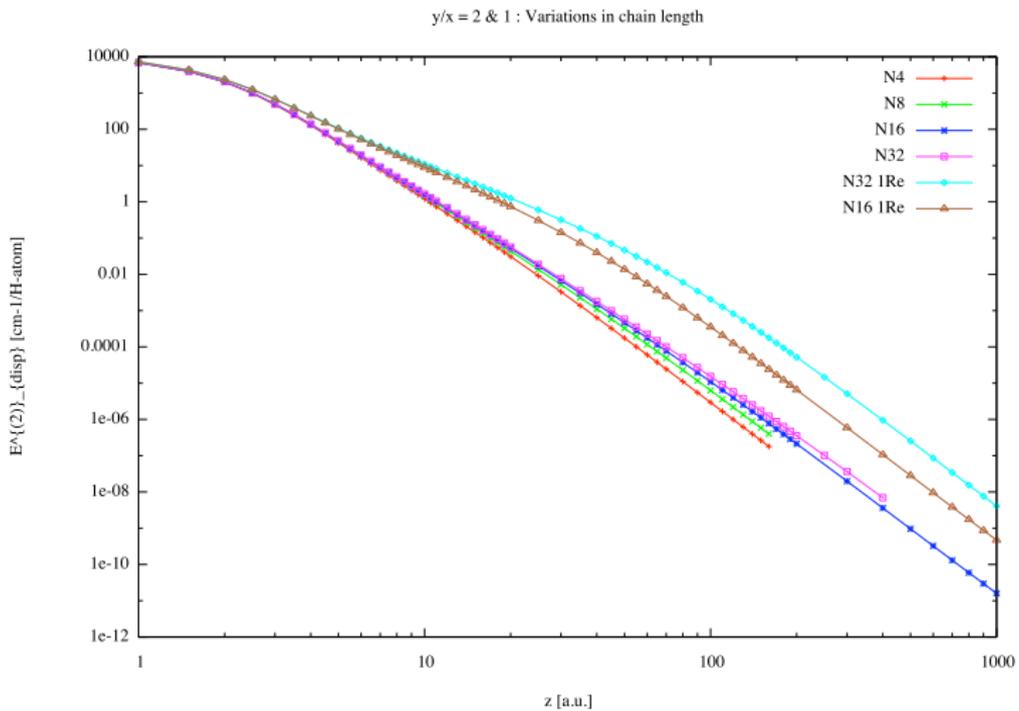
ξ	(H ₂) ₂	(H ₂) ₄	(H ₂) ₈	(H ₂) ₁₆	(H ₂) ₃₂
2.0	0.458	0.409	0.382	0.370	0.366
1.5			0.305	0.280	0.270
1.25				0.202	0.183
1.0				0.099	0.057

Interactions between distorted chains.



Variations with chain length





Power-law behaviour of $E_{\text{disp}}^{(i)}$ in the region from

ξ	$(\text{H}_2)_2$	$(\text{H}_2)_4$	$(\text{H}_2)_8$	$(\text{H}_2)_{16}$	$(\text{H}_2)_{32}$
4.0					
2.0		5.20	4.99	4.89	4.84
1.5				4.58	4.50
1.25				4.20	4.09
1.0				3.52	3.17

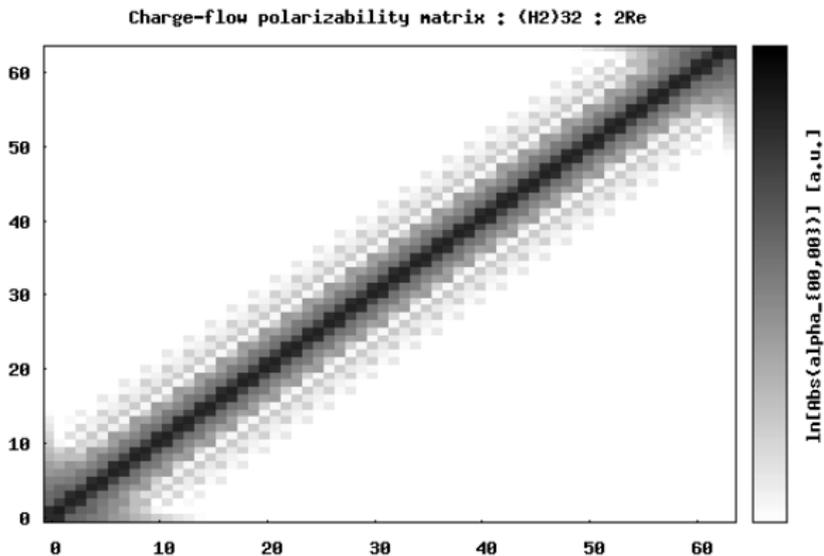
Why??? The exact (expanded) dispersion energy is not

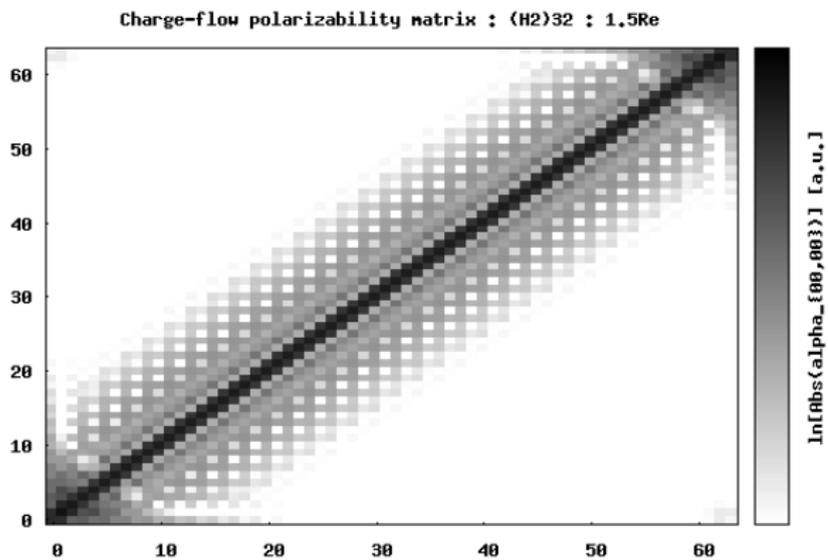
$$E_{\text{disp}}^{(2)} = -\frac{1}{\pi} \sum_a \sum_b T_{tu}^{ab} T_{t'u'}^{ab} \int_0^\infty \alpha_{tt'}^a(i\omega) \alpha_{uu'}^b(i\omega) d\omega$$

but it is

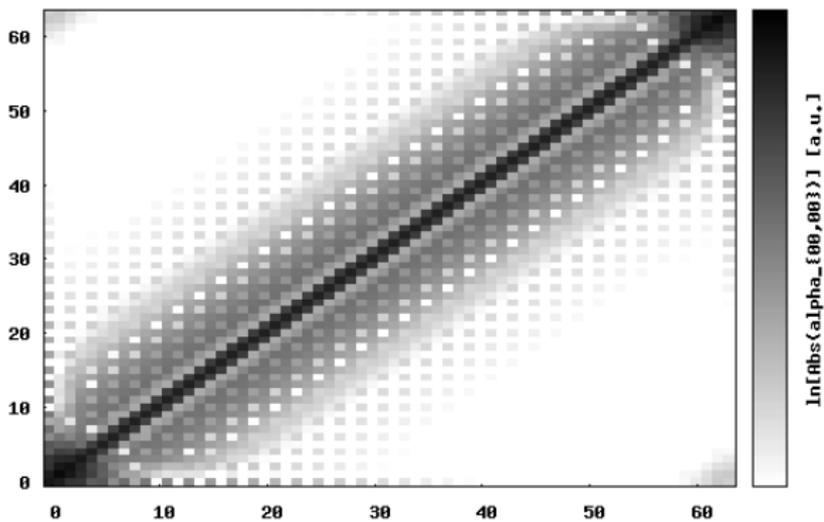
$$E_{\text{disp}}^{(2)} = -\frac{1}{\pi} \sum_{a,a'} \sum_{b,b'} T_{tu}^{ab} T_{t'u'}^{a'b'} \int_0^\infty \alpha_{tt'}^{aa'}(i\omega) \alpha_{uu'}^{bb'}(i\omega) d\omega$$

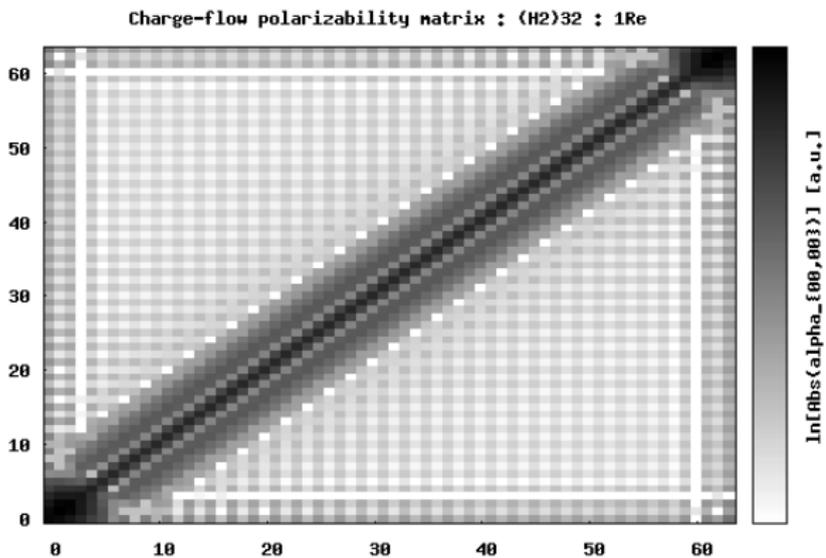
$(H_2)_{32}$: Charge-flow terms



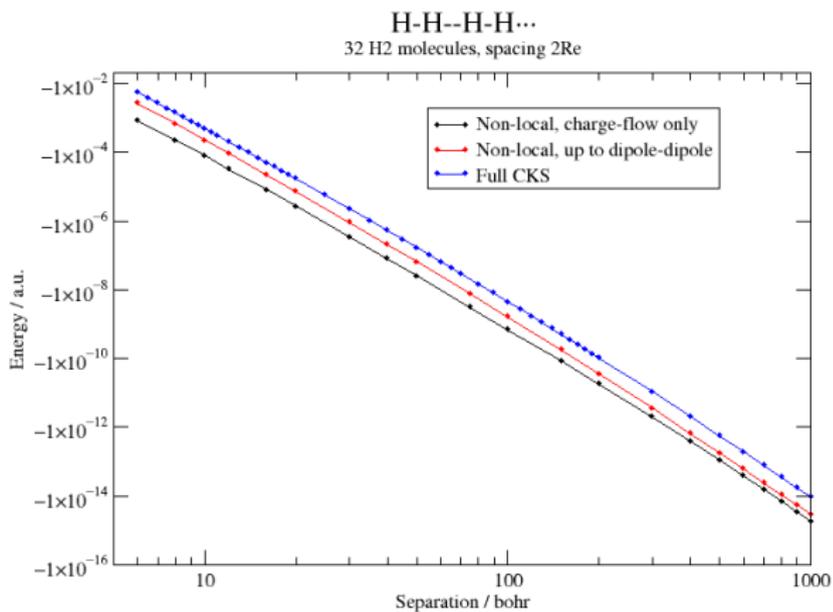


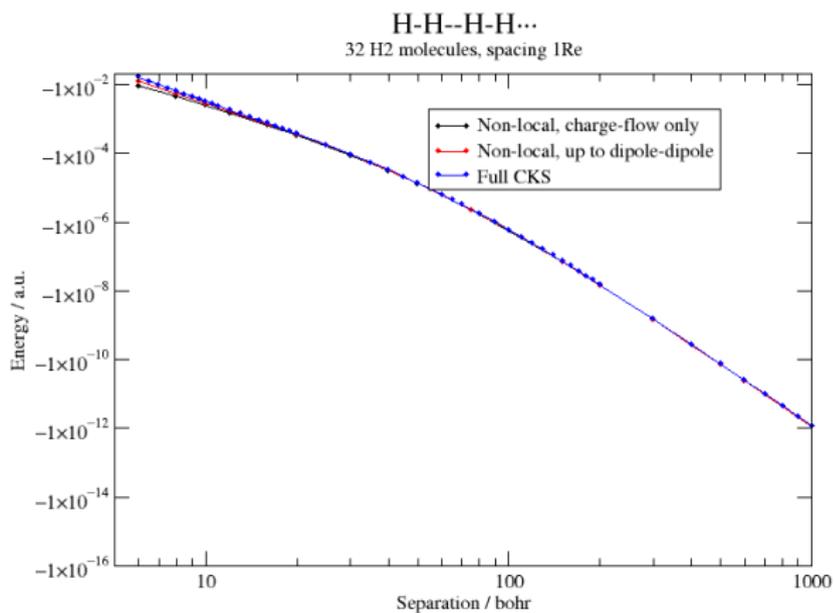
Charge-flow polarizability matrix : (H2)32 : 1.25Re





$(\text{H}_2)_{32}$: Dispersion coefficients





Credits

- ▶ Work on infinite chains that started it all: Ali Alavi & James Spencer
- ▶ Implementation of non-local dispersion coefficients and code to use them: Anthony Stone

And a very big thanks to Mike!

Anthrapyrалene

