Symmetry,

(Electronic Structure)

and **Bonding**

2012 Special Final Edition

Hierarchical Organization of the Universe

- ⋆ elementary particles
  (neutrinos, electrons, protons, . . .)
- ⋆ nuclei
- ⋆ atoms
- ⋆ molecules (H_2, H_2O, . . .) — **chemistry**
- ⋆ biomolecules (peptides, DNA, . . .)
- ⋆ unicellular organisms — **life**
- ⋆ plants, animals
- ⋆ whales, chimps, humans . . . — **consciousness**
- ⋆ societies, ecosystems
- ⋆ www and the "Technological Singularity"?

Physical chemistry:

observe and explain how atoms interact and combine to form molecules and

how molecules interact and combine to form substances (gases, liquids, solids).

Chemists need good models for atoms.

Atoms are . . .

- **Point-like hard spheres** — $pV = nRT$
- **Compressible sticky spheres**
  — van der Waals equation, liquids, solids.
- **Spheres with N “hooks”** ($N = 4$ for C)
  — molecular formula, Lewis theory

We can do better than that . . .

Why should a chemist know anything about quantum mechanics (QM)?

1. We need better models of atoms than "*compressible sticky sphere*".

2. Classical mechanics (CM) fails *entirely* to describe electrons in atoms and molecules.

3. QM gives a "*perfect*" description.

4. One must know the fundamentals in order to be able to innovate or improvise. Chemists need QM for the same reasons a pilot needs to know about gravity, acceleration, friction, . . .

Symmetry:

Molecules having high symmetry are simpler to understand, more important in theory.

Benzene, ferrocene, C_{60}, $Cr(CO)_6$, Ar_{13}, …

Interaction Potentials

$\mathrm{H} \cdots \mathrm{H}$

$\mathrm{C} \cdots\cdots \mathrm{O}$

$\mathrm{Ar} \cdots\cdots\cdots\cdots \mathrm{Ar}$

$\mathrm{CH_4} \cdots\cdots\cdots\cdots \mathrm{CH_4}$

Earth················René

Gravitational potential, U_G:

$$U_G = \frac{-GM_1M_2}{R}$$

$$G = 6.67 \times 10^{-11} \quad (SI \;\; units)$$

$$M_1 = 5.98 \times 10^{24}\, kg$$

$$R = 6.37 \times 10^{6}\, m$$

$$M_2 \approx 70\, kg$$

$$U_G = -4.38 \times 10^{9}\, J$$

Suppose we want to put this person far, far away, in orbit. We must accelerate him to a KE of precisely $4.38 \times 10^9\ J$ to overcome the binding energy.

$$\begin{aligned} K &= \frac{1}{2}mv^2 \\ v &= (2K/M_2)^{1/2} \\ &= (-2U_G/M_2)^{1/2} \\ &= (2GM_1/R)^{1/2} \\ &= 1.12 \times 10^4\, m/s \\ &= 40,287\, km/h \end{aligned}$$

This is the *escape velocity* of objects on Earth.

How do we calculate the energy needed to separate two atoms?

Here's how a typical atom$\cdots$atom interaction potential $U(r)$ looks like:

- different for every molecule "AB"
- unlike U_G, no simple mathematical formula
- very hard to obtain
- $D_e \approx 1$ to 10 eV in most molecules
  $(1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$

U_G for two I atoms in the I_2 molecule:

$$M_1 \;=\; M_2 = 127 \times 1.66 \times 10^{-27}\, kg$$

$$R \;\approx\; R_e(I_2) = 2.67\,\text{Å} = 2.67 \times 10^{-10}\, m$$

$$D_e(I_2) \;=\; 1.54\, eV = 2.47 \times 10^{-19}\, J$$

$$U_G \;=\; 1.66 \times 10^{-40}\, J$$

U_G is 7×10^{22} times smaller than D_e !

The I$\cdots$I interaction (the bond) is due to a complex combination of many electrostatic interactions between two nuclei with +53 charge, and 106 e^- with charge −1.

Interaction of two point charges Q_1 and Q_2 separated by a distance r:

$$U_{elec.} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$$

In **atomic units** (a.u.), not to be confused with atomic mass units (a.m.u.),

$$m_e = 1$$

$$h = 2\pi \quad (Planck's\ \ constant)$$

$$4\pi\epsilon_0 = 1$$

$$Q_e = -1$$

a.u. of energy = 27.211 eV = 4.360×10^{-18} J

a.u. of length= 0.52918 Å = 0.52918×10^{-10} m

In one iodine molecule, *if* the 2 nuclei and 106 e^- were fixed in space, we would have

$$U = \sum_{i=2}^{i=108} \sum_{j=1}^{j=i-1} \frac{Q_i Q_j}{r_{ij}}$$

but ...

- nuclei and e^- move constantly,
- their KE is not zero,
- their positions, speeds, and KE can **not** be obtained by Newton's equations (CM)

Consider two e$^-$ 2.67 Å apart:

$$U_{elec.} = \frac{(-1)(-1)}{2.67 \div 0.529177} = 0.1982\, a.u.$$

$$= 5.39\, eV$$

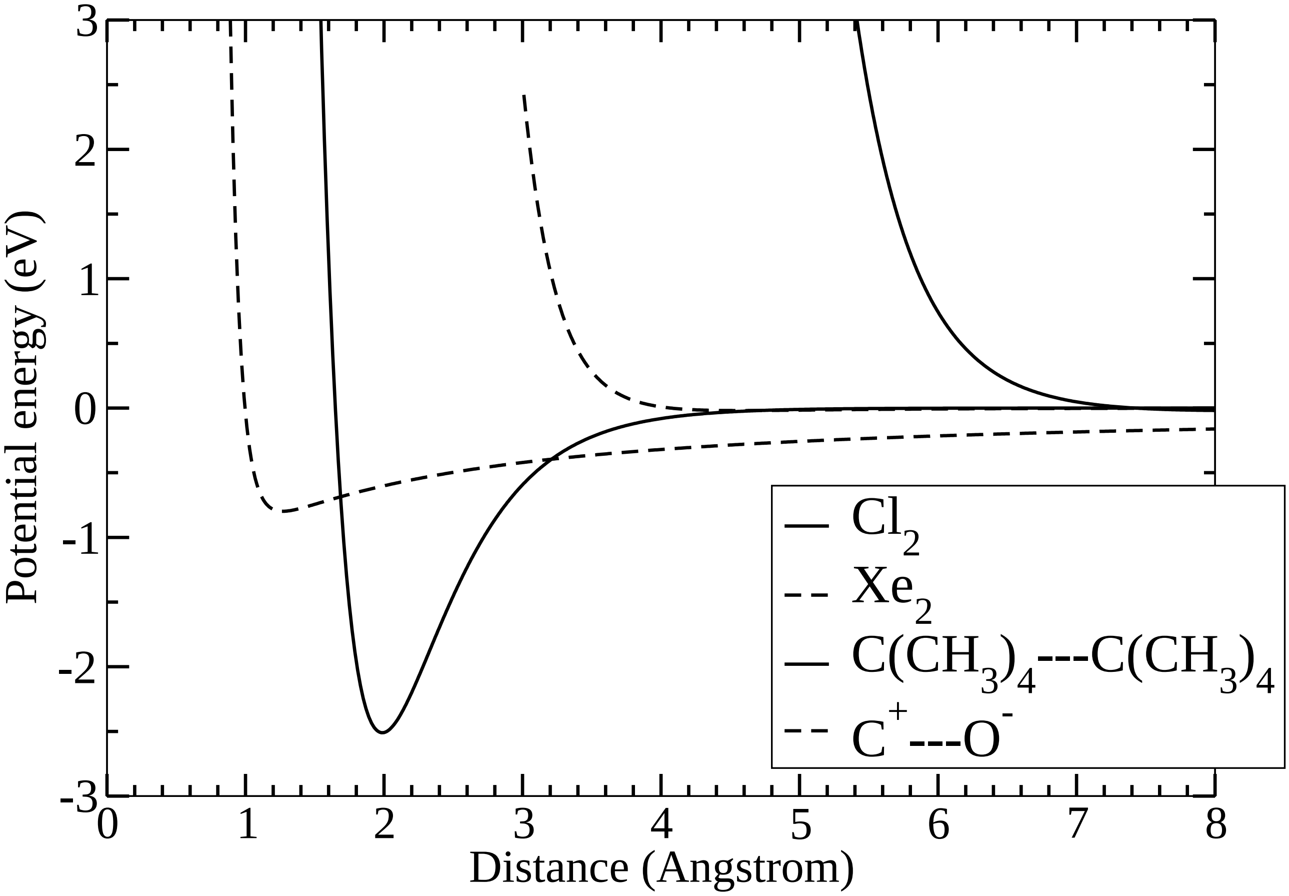
Compare I_2 to two separated I atoms: we have $53^2 + 53 + 53 + 1 = 2916$ pair interactions that were zero in the separated atoms. In I_2, these interactions are all on the order of 5 eV. Add to that *changes* to 108 KE's and to 2862 interactions $(2 \times (54 \times 53/2) = 2862)$. These energies all add up to …

… 1.5 eV, the D_e of I_2

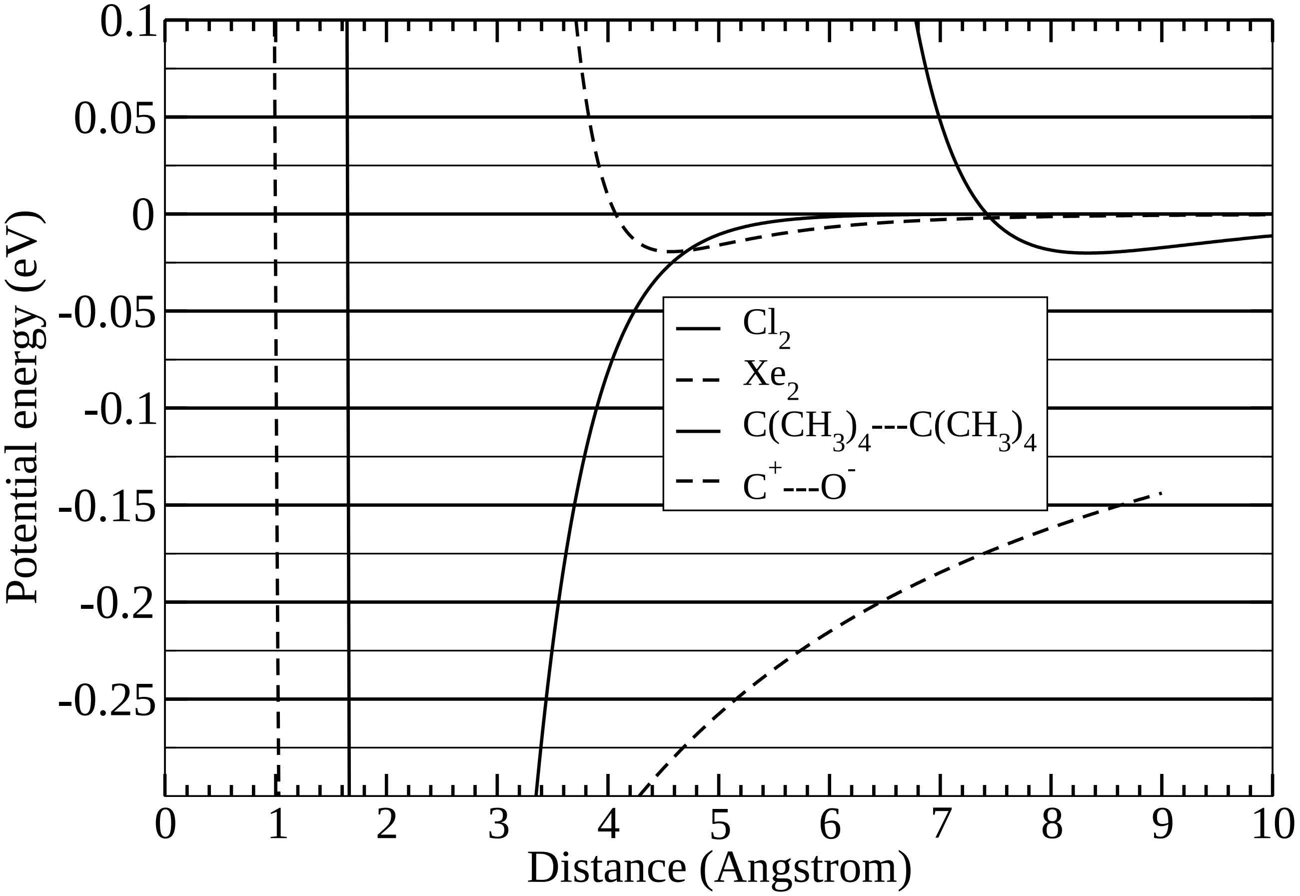
The next 2 pages have potential curves that illustrate different types of interactions

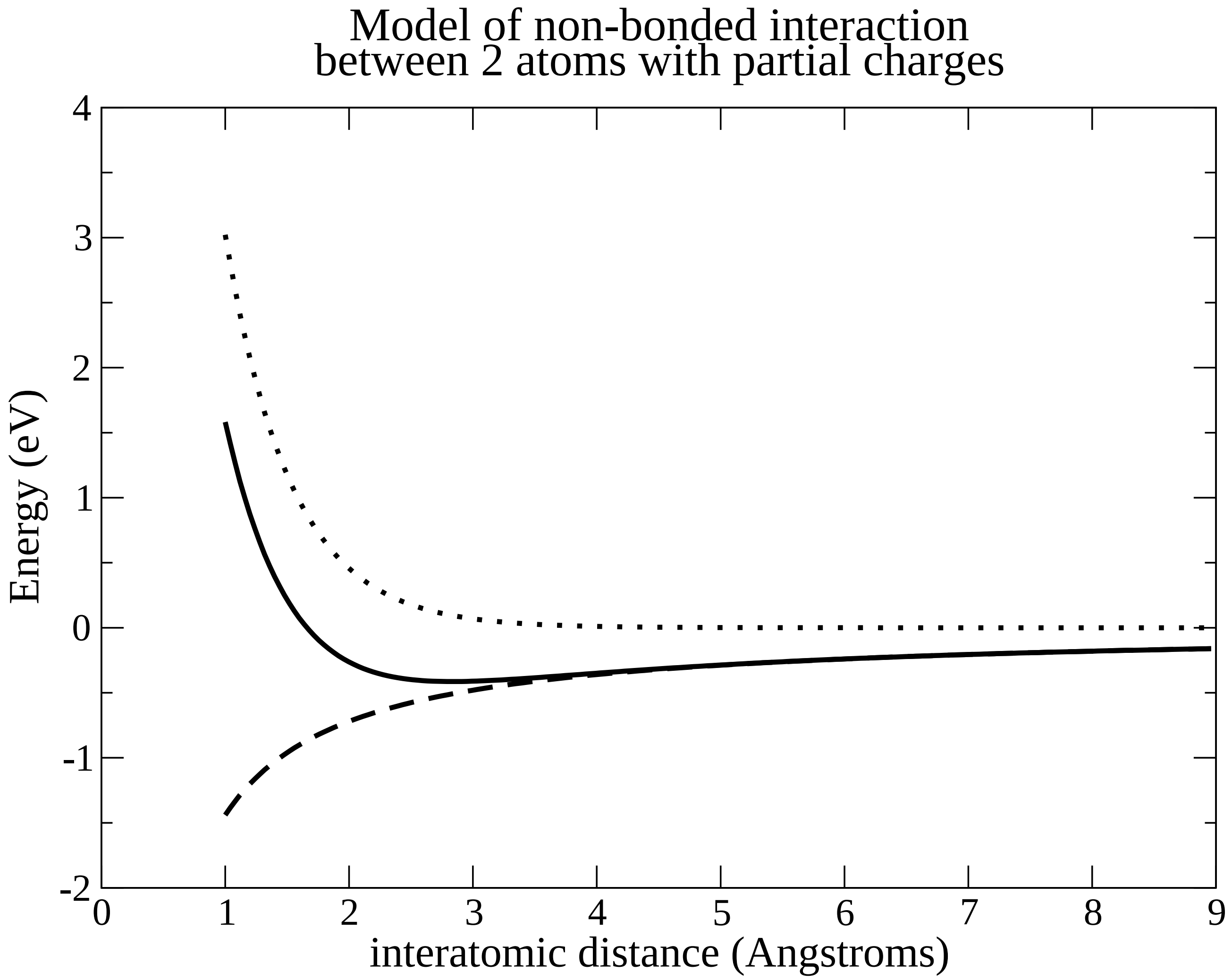
- covalent (Cl_2)
- nonbonded ionic ($C^{+\delta} \cdots O^{-\delta}$)
- dispersion (Xe_2, neopentane dimer)
- ionic bond (NaCl)

Representative interaction energy curves



Representative interaction energy curves




Model of non-bonded interaction
between 2 atoms with partial charges
Energy (eV)
4
3
2
1
0
-1
-2
0
1
2
3
4
5
6
7
8
9
interatomic distance (Angstroms)

The next pages have experimentally determined bond dissociation energies D_0, equilibrium bond lengths R_e, and dimer interaction energies.

Memorize them to an accuracy of ± 50% or ±1 eV (whichever is smaller) for energies, and ±0.1 Å for R_e.

You don't have to memorize the following: BN, BF, CF, FN, FO; LiH, NaH, KH, RbH, LiF, NaF, KF, RbF; Sc_2, Ti_2, V_2, Cr_2, Mn_2

D_0 and R_e of selected diatomic molecules

	D_0 (eV)	R_e (Å)
H_2	4.52$^{(a)}$	0.7413
Li_2	1.05	2.67
Be_2	0.103	2.45
B_2	3.10	1.59
C_2	6.3	1.31
N_2	9.79	1.094
O_2	5.17	1.207
F_2	1.65	1.412
Ne_2	0.004	3.09

(a) The dissociation energy of a molecule D_0 is smaller than its D_e (for, H_2 4.52 vs 4.75 eV) for reasons we'll see later.

D_0 and R_e of selected diatomic molecules

	D_0 (eV)	R_e (Å)
B_2	3.10	1.59
C_2	6.3	1.242
BN	4.03	1.281
CN	7.81	1.172
N_2	9.79	1.094
CO	11.16	1.128
BF	7.85	1.263
NO	6.54	1.151
CF	5.72	—
O_2	5.17	1.207
FN	3.56	—
FO	2.30	—
F_2	1.65	1.412

D_0 and R_e of selected diatomic molecules

	D_0 (eV)	R_e (Å)
H_2	4.52	0.7413
Li_2	1.05	2.67
Na_2	0.74	3.08
K_2	0.520	3.92
Rb_2	0.495	4.21

D_0 and R_e of selected diatomic molecules

	D_0 (eV)	R_e (Å)
LiH	2.47	1.595
NaH	1.92	1.887
KH	1.81	2.244
RbH	1.73	2.367
LiF	5.98	1.564
NaF	5.38	1.926
KF	5.16	2.172
RbF	5.12	2.270

D_0 and R_e of selected diatomic molecules

	D_0 (eV)	R_e (Å)
LiCl	4.86	2.02
NaCl	4.27	2.36
KCl	4.49	2.667
RbCl	4.43	2.787
NaBr	3.81	2.50
KBr	3.94	2.821
NaI	3.15	2.71
KI	3.37	3.048

D_0 of selected diatomic molecules, in eV

F_2 1.65	Cl_2 2.52	Br_2 2.00	I_2 1.57	
Sc_2 1.04	Ti_2 1.4	V_2 2.75	Cr_2 1.44	Mn_2 0.3
Fe_2 1.15	Co_2 (1.3)	Ni_2 2.042	Cu_2 2.03	Zn_2 0.3

Average bond energies (eV)

H—C	H—N	H—O	H—S
4.29	4.03	4.81	3.81
C—C	C=C	C≡C	
3.60	6.33	8.68	
N—N	N=N	N≡N	
1.69	4.33	9.80	
C—N	C=N	C≡N	
3.16	6.37	9.23	
C—O	C=O	Si—O	
3.73	7.63	3.83	
N—O	N=O	O—O	O=O
2.30	6.12	1.47	5.16
S—S	P—O	P=O	Si—Si
2.49	3.47	5.64	2.30

Pairwise interaction energies (kJ/mol) of selected dimers

Ne_2	Ar_2	Xe_2	$(CH_4)_2$	$(CCl_4)_2$	
0.4	1.1	2.1	1.4	4.5	
Linear alkanes, Cn—Cn, with					
n=2	n=4	n=5	n=6	n=12	n=18
2.5	3.8	4.9	6.4	12	17

1 eV = 96.5 kJ/mol.
For chemical bonds, $100 \lessapprox D_0 \lessapprox 1000$ kJ/mol

At 298 K, $RT = 2.5$ kJ/mol.
At 298 K, butane is a gas ($T_b = -0.5°\mathrm{C}$), pentane is a liquid ($T_b = 36°\mathrm{C}$) and CCl_4 is a liquid ($T_b = 77°\mathrm{C}$).

Notes

Most of the data in these tables are from the CRC Handbook of Chemistry and Physics 78th Edition

The experimentally determined dissociation energy of H_2 is 4.4780(76) eV, see Phys. Rev. Lett. 68 (1992) 2149. The best quantum mechanical calculation on H_2 gives 4.4780(74) eV. That's what I meant by "QM is perfect".

For Be_2, see Science 19 June 2009: Vol. 324 no. 5934 pp. 1548-1551

See Inorg Chem 38 (1999) 4696-4699 for data on heavy alkali dimers

Calculating $U(r)$ or D_e

- full blown QM calculation (for experts only)
- physical models, based on CM or QM, to reduce complexity

Types of interactions

- covalent bond*
- ionic bond
- steric repulsion*
- nonbonded charge-charge (q-q)
- charge-dipole (q-μ)
- dipole-dipole (μ-μ)
- dispersion ($\mu_{in.}$-$\mu_{in.}$)

* there is no good classical model for these interactions, QM is needed

Classical model of electrostatic interactions

Atoms and molecules have charge distributions that can be described approximately with . . .

- point charges, q
- electric dipoles, μ
- quadrupoles, octupoles, etc.

Electric Dipole

2 charges $+q$ and $-q$ separated by a distance d produce a **dipole** equal to $\mu = qd$, by definition.

$$\begin{aligned} 1 \text{ a.u. of dipole} &= 2.5412 \text{ Debye} \\ &= 2.5412 \times 3.336 \times 10^{-30} \text{ C m} \end{aligned}$$

<u>Point dipole</u> of 1 Debye: a fictitious system with 2 charges $q = \pm(1 \text{ Debye} \div d)$ that we take to the limit $d \to 0$ $(q \to \infty)$

q-q interaction $\quad \propto 1/r$

take $q_1 = -q_2 = 1$

and $r = 2\text{Å} \div 0.52918 = 3.78$ a.u.

$U_{qq} = 0.2646$ a.u. $= 7.2$ eV

q-μ interaction $\quad \propto 1/r^2$

take $q = +1$,

and $r = 3.78$ a.u., $\mu = 1$ a.u. (2.54 Debye)

$U_{q\mu}$ also depends on the **size** of the dipole, and its **orientation**. Take a dipole having $q = \pm 1$ and $d = 1$ a.u.

- $\uparrow \qquad U_{q\mu} = 0$
- $\rightarrow \qquad U_{q\mu} = 0.0712$ a.u. $= 1.93$ eV
- $\leftarrow \qquad U_{q\mu} = -1.93$ eV

Here's one way to show that $U_{q\mu} \propto 1/r^2$.

Take a point charge of +1 and a 1 a.u. dipole of size 1, separated by distance r, let $r = 4, 8, 16$, and calculate U in each case.

$$U = -1/3.5 + 1/4.5 = -0.0635$$

$$U = -1/7.5 + 1/8.5 = -0.0157$$

$$U = -1/15.5 + 1/16.5 = -0.00391$$

Calculate ratios of U as you **halve** the distance between the charge and the dipole.

$0.0635/0.0157 = 4.04$;
$0.0157/0.00391 = 4.02 \approx 4$.

μ-μ interaction $\quad \propto 1/r^3$

Take two dipoles $\mu = 1 \times 1 = 1\,\text{a.u.}$,

and $r = 3.78$ a.u., as before.

$U_{\mu\mu}$ depends on the relative orientation.

$\rightarrow\ \rightarrow \qquad U_{\mu\mu} = -0.0398$ a.u.$= -1.08$ eV

$\rightarrow\ \leftarrow \qquad U_{\mu\mu} = +1.08$ eV

$\uparrow\ \downarrow \qquad U_{\mu\mu} = -0.48$ eV

$\uparrow\ \rightarrow \qquad U_{\mu\mu} = 0$

Do as before: two dipoles of 1 ($q = 1$, $d = 1$) separated by $r = 4, 8, 16, 32$

$$-1/3 + 2(1/4) - 1/5 = -0.03333$$

$$-1/7 + 2(1/8) - 1/9 = -0.003968$$

$$-1/15 + 2(1/16) - 1/17 = -0.0004902$$

$$-1/31 + 2(1/32) - 1/33 = -0.00006109$$

the ratios are

$0.03333/0.003968 = 8.40$
$0.003968/0.0004902 = 8.09$
$0.0004902/0.00006109 = 8.023 \approx 8$

so $U_{\mu\mu} \propto 1/r^3$

$\mu_{in.}$-$\mu_{in.}$ interaction, or, **dispersion** $\propto 1/r^6$

The "in." can stand for "instantaneous" or "induced".

Take a Ar atom. On *average*, it has no net charge ($q = 0$), no net dipole ($\mu = 0$), no quadrupole, no octupole, etc., because its electronic distribution has perfect *spherical symmetry*.

But e$^-$ move constantly. Suppose at some time 10 e$^-$ are on one side of the Ar atom and 8 e$^-$ are on the other side. The radius of Ar is 1Å or 2 a.u., so a *typical* instantaneous dipole would be 2 a.u. Suppose we have a second Ar atom a distance $r = 8$ a.u. away: its e$^-$ will be "pulled" (or "pushed") by the dipole on the first atom. The magnitude of that effect is roughly 0.9 eV (the charge-dipole potential). By comparison, the intra-atomic forces are much bigger, they produce a ionization energy of 15.8 eV for Ar. So:

(a) on average, the induced dipole $\mu_{induced}$ is much less than 2 a.u., and typically $U\mu_{in.}\mu_{in.}$ is much smaller than $U\mu\mu$ (permanent dipoles interaction)

(b) $\mu_{induced}$ gets smaller as r increases, so $U\mu_{in.}\mu_{in.} \propto 1/r^n$ with $n > 3$. As it turns out, $n = 6$.

Note: the binding energy of the Ar dimer is 1.19 kJ/mol, J Phys Chem A 109 (2005) 11015.

To recap different types of interactions.

- $qq \quad \propto 1/r \qquad \approx 10$ eV or less
- $q\mu \quad \propto 1/r^2 \qquad \approx 3$ eV or less
- $\mu\mu \quad \propto 1/r^3 \qquad \approx 1$ eV or less
- $\mu_{in.}\mu_{in.} \quad \propto 1/r^6 \qquad \approx 0.005$ eV–0.05 eV
  it's never zero!

Dispersion interactions $\mu_{in.}-\mu_{in.}$ are always present, are typically on the order of 1–5 kJ/mol for small molecules, and that's why small molecules are normally gases at 300 K ($RT = 2.5\,kJ/mol$).

Dispersion interactions between two big molecules are much bigger, and are roughly proportional to the contact area because all $1/r^6$ interactions are negligible except for the smallest r, ie, *at* the dividing surface between the molecules.

Dispersion energy $U_{\mu_{in.}\mu_{in.}} \propto 1/r^6$: why?

We saw already that $U_{\mu\mu} \propto 1/r^3$. But that's for the case of two *permanent* dipoles in a *fixed relative orientation*.

For the dispersion case, one dipole is induced by the other. The size of the induced dipole must surely decrease as r increases. The $\mu_{induced}$ is due to a *force* exerted by the instantaneous dipole of the first atom on the charges (nucleus and electrons) of the second atom. The **potential** felt by charges and due to a dipole is $\propto 1/r^2$ (see the $q\mu$ slides). The corresponding **force** is the negative of the derivative of that potential[a]: $-d/dr(1/r^2) = 2/r^3$. So, the force between the instantaneous dipole and the nucleus and electrons of the second atom is $\propto 1/r^3$, and **the induced dipole is also** $\propto 1/r^3$.

The instantaneous dipole does not depend on the distance between the two atoms r, it is found even in isolated atoms as a result of fluctuations in the positions of electrons, so count that as $\propto 1/r^0$ (no r dependence). Putting the 3 things together, we find for the dispersion potential

$$
\begin{aligned}
U_{dispersion} &\propto \frac{\mu_{instantaneous} \;\; \mu_{induced}}{r^3} \\
&\propto (1/r^0)(1/r^3)/(1/r^3) \\
U_{dispersion} &\propto 1/r^6
\end{aligned}
$$

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[a] No matter what kind of interaction it is, the force along x is the negative of the derivative of the potential with respect to x, always.

The next few graphs show

$$U(r) = Ae^{-a(r-r_0)/r_0} - C_n/r^n$$

to illustrate how electrostatic interaction energy curves between atoms and molecules look like.

Dipoles and geometries of a few small molecules and “atomic charges” deduced from them:

water: $\mu = 1.85$ Debye $= 0.73$ a.u.,
$R_{OH} = 0.958$ Å , $\theta = 104.5^\circ$
$q_O = -0.66 \quad q_H = +0.33$

NaCl: $\mu = 3.35$ a.u., $R_e = 2.361$ Å ,
$q = \pm 0.75$

HCl: $\mu = 0.43$ a.u., $R_e = 1.275$ Å ,
$q = \pm 0.18$

Quantum Mechanics (QM) (or wave mechanics, or matrix mechanics)

- developed in 1900-1930
- it explained
  blackbody radiation
  photoelectric effect
  electron diffraction
  hydrogen spectrum
- 2 key ideas:
  energy is quantized
  waves (e.g., light) sometimes behave like particles, and particles (e.g., e^-) sometimes behave like waves = **wave-particle duality**

Black body radiation

A black body is a solid metal sphere with a *small* cavity and *small* aperture, as shown below.

- heat the black body to temperature T
- light comes out (many frequencies)
- the spectrum of that light, $I(\nu)$ looks like this …

Using the known laws of electromagnetism and thermodynamics gives a **completely different** spectrum than the observed one

In 1900, Planck managed to explain the observed spectrum $I(\nu)$, but only after assuming that light consists of energy packets

$$E = h\nu$$

Light (a wave) is behaving as if it were made of particles

Photoelectric effect

The e^- traveling through space from the metal plate to the detector close the circuit and produce a current that can be measured.

The applied potential ΔV is set just big enough to stop the current: this way, we find out the KE of e^- as they left the metal.

current $\propto$ number of e^- emitted, so we

- Input light of intensity I and frequency ν
- detect N e^- with kinetic energy K

The main results can be expressed with 3 plots:

(1) Fix I: $N = 0$ as long as $\nu < \nu_0$, and N does not vary with ν passed the initial jump.

(2) Fix ν ($\nu > \nu_0$): $N \propto I$

(3) Fix I, vary ν ($\nu > \nu_0$): $K \propto \nu$

How can those things be explained?

1. light is made of **photons** having $E = h\nu$
2. when **one** photon collides with **one** e^-, it transfers all of its energy $(h\nu)$ to the e^-
3. the e^- is bound to the metal by $W = h\nu_0$: if $h\nu > h\nu_0$, the e^- acquires enough energy to escape with kinetic energy $K = h\nu - h\nu_0$
4. the energies of several low-energy photons can not be pooled together to kick out a single e^-: $N_e = 0$ when $\nu < \nu_0$ even when I is very large.

The last point is analogous to the situation in chemical kinetics: *termolecular elementary reactions are very unlikely because 3-body collisions are very rare.*

Light behaves as a collection of particles.

Electron diffraction

A beam of e^- is directed at a plate with two slits of width a separated by a distance b.

The e^- that pass through the slits hit a photographic plate (a detector).

The pattern formed by the e^- is just like what you would get if a *wave* had gone through the two slits! It is a *diffraction pattern*.

The diffraction pattern is observed even when the beam intensity is very low, e.g., one electron per hour!

So . . .

Beams of e^-, and even individual e^-, behave as if they were a wave

Light, a wave, sometimes acts as if it is made of particles (photons).

Matter, for ex. electrons, sometimes acts as if it were a wave with wavelength λ*.*

DeBroglie Wavelength λ

Energy of a photon: $E = h\nu = hc/\lambda$

Mass-energy relation for a photon: $E = m_0 c^2$
Then,

$$hc/\lambda = m_0 c^2$$

$$h/\lambda = m_0 c = p$$

Suppose that is also true for a particle,
$m_0 \Rightarrow m$, $c \Rightarrow v$:

$$\lambda = h/p = h/mv$$

$h = 6.6262 \times 10^{-34}\, J\, s = 2\pi$ a.u.

Boltzmann Equation

$$\frac{n_i}{n_j} = \frac{g_i}{g_j}\ \exp[-(\epsilon_i - \epsilon_j)/kT]$$

n_i: number of molecules having energy ϵ_i

T: temperature, in Kelvin

k: Boltzmann constant

g_i: degeneracy of energy level i

Quantum Mechanics (QM) vs Classical Mechanics (CM)

QM is more general: CM can be derived from QM

CM is a lot simpler: use it *when you can*

CM becomes increasingly accurate as …

- … the size of objects $\nearrow$,
- the mass of objects $\nearrow$,
- and temperature $\nearrow$

When does CM fail? When do we need QM?

- when λ of a particle is sufficiently large **compared** to the system or phenomenon we are interested in. This normally happens when light objects (small $m \Rightarrow$ big λ) move inside small systems (typically a few Å)

- when the smallest energy differences $(\epsilon_{j+1}-\epsilon_j)$ between the states of an atom or molecule are not small compared to k_BT. The lower T is, the bigger "**quantum effects**" are.

Example:

Take an e$^-$ with speed $v = c/137 = 1\,\text{a.u.}$

In a.u.: $p = mv = 1\,\text{a.u.}$ of mass × $1\,\text{a.u.}$ of speed $= 1\,\text{a.u.}$, and $h/2\pi = \hbar = 1$. So

$$\lambda = h/p = 2\pi\hbar/1 = 2\pi\,\text{a.u.}$$

$$= 2\pi \times 0.5291771\,\text{Å/a.u.} = 3.3\,\text{Å}$$

This e$^-$ in a molecule: we need QM

This e$^-$ going through a 1 mm wide slit:
CM works just fine

As $v \nearrow$, CM becomes better; but as v approaches c, **relativistic effects** become important.

Calculate the DeBroglie wavelength λ for

1) an e^- with a KE of 0.1 eV;
2) " " " " " " 10 eV;
3) " " " " " " 1000 eV;

4) a H atom with a KE of 0.12 eV ("H in H_2");

5) H_2 molecule with KE of 0.026 eV ("H_2 at rt");
6) H_2 at 50 K, with KE of 0.0042 eV;
7) H_2 at 2000 K, with KE of 0.172 eV;

8) a N_2 molecule with a KE of 0.026 eV;

9) a protein, MW=10000 amu, KE=0.026 eV

A string is stretched between two points a distance d apart. If you pluck the string, a standing wave is quickly established. If we take a snapshot at time t, we see a sine function with $\lambda = 2d/n$, where n is an integer. Any other type of wave motion in the string, ie with n *not* an integer, quickly fades away due to destructive interference. The **wave equation** is a differential equation that describes the amplitude $\psi = \psi(x)$ of the standing wave along x

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)\psi$$

From λ to Schrödinger's eqn

$$E = mv^2/2 + V = p^2/2m + V$$

$$p = [2m(E - V)]^{1/2}$$

$$\lambda = h \div [2m(E - V)]^{1/2}$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = \left(\frac{-4\pi^2\ [2m(E - V)]}{h^2}\right)\psi(x)$$

$$\frac{-h^2}{8\pi^2 m} \quad \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

This is S̈ time-independent equation.

We will look at solutions to the S̈ equation for two model systems:

the free particle (FP): $V(x) = 0$ everywhere

the particle in a box (PIB):

$$V(x) = 0 \ \text{ for } \ 0 < x < a$$
$$V(x) = \infty \quad \text{elsewhere}$$

Normally, a course in quantum chemistry would also deal with the $\ddot{\text{S}}$ equation for

a particle in a finite-depth box,

$$V(x) = 0 \quad \text{for} \;\; 0 < x < a,$$
$$V(x) = C > 0 \quad \text{elsewhere}$$

a particle in a ring

$$V(x, y) = 0, \quad x^2 + y^2 = \text{a constant}$$

rigid rotor $V(\theta, \phi) = 0$, (θ, ϕ) on a sphere

a harmonic oscillator $V(x) = x^2$

the H atom, $V(x, y, z) = V(r) = 1/r$

Free Particle (FP) in 1D

$V(x) = 0 \quad (V \text{ is constant})$

$F = -\frac{dV}{dx} = 0$ everywhere

Classical Mechanics:

$$F = m\frac{d^2x}{dt^2} = 0$$

Find a function $x(t)$ satisifying that equation.

$$x(t) = x_0 + vt$$

x_0: initial position (a constant)
v: speed (another constant)
$x(t)$ defines a **trajectory**

FP, Quantum Mechanics:

$$V(x) = 0$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

what function ψ equals its own second derivative within a constant?

- $A\sin(kx)$ and $B\cos(kx)$ ...
- or A_+e^{ikx} and A_-e^{-ikx}

These 2 pairs of functions are interchangeable bc

$$\cos x = (e^{ix} + e^{-ix})/2$$
$$\sin x = (e^{ix} - e^{-ix})/2i$$

The solutions to the FP S̈ equation are

$$\psi(x) = A_+e^{ikx} = A_+\left[\cos(kx) + i\sin(kx)\right]$$
$$\psi(x) = A_-e^{-ikx} = A_-\left[\cos(kx) - i\sin(kx)\right]$$

You can plot $Re(\psi)$ or $Im(\psi)$, they both look like sine waves extending to infinity in both directions with $\lambda = 2\pi/k$.

$$\begin{aligned}\frac{d^2}{dx^2}\left(A_+e^{ikx}\right) &= -k^2\ A_+e^{ikx}\\ &= \frac{-2m}{\hbar^2}E\ A_+e^{ikx}\end{aligned}$$

so, the energy is

$$E = (\hbar k)^2/2m$$

k can be *any* positive real number. So any energy is possible: the energy of a FP is a *continuous* variable, is it *not quantized*. The momentum of a FP, $p = \sqrt{2mE}$, is also a continuous variable.

What is the meaning of a wavefunction $\psi(x)$, a solution to the $\ddot{\text{S}}$ equation?

Max Born (1926):

$\psi\psi^* dx$ is the probability of finding the particle between $x - dx/2$ and $x + dx/2$.

The probability of finding the particle *somewhere* is 1, so

$$\int_{-\infty}^{+\infty} \psi\psi^* dx = 1$$

This is called the **normalization** of the wavefunction.

For the FP

$$\psi\psi^* dx = A_+ e^{ikx} \, A_+ e^{-ikx} \, dx$$

$$= (A_+)^2 dx$$

The FP has a *uniform probability distribution*, just as in CM.

Note:
The wavefunction of the FP is a bit special: it can not be normalized. But if we have a beam of free particles of intensity I (say, I particles per meter), we can normalize ψ to reproduce that I.

Particle in a Box (PIB) in 1D

$V(x) = +\infty$ except for $0 < x < a$ where $V(x) = 0$

$\psi(x)$ must be zero when $x < 0$ and $x > a$ or else the energy would be infinite $(E = V + K,\ K > 0)$.

In the region $0 < x < a$ we have almost the same situation as for the FP. In order to solve the S̈ equation, we are looking for functions $\psi(x)$ that equal their own second derivative to within a multiplicative constant:

$$\psi(x) = -\frac{\hbar^2}{2mE}\ \frac{d^2}{dx^2}\,\psi(x)$$

As for the FP, we could use either $Ae^{\pm ikx}$, or $A\sin(kx)$ and $B\cos(kx)$. As it turns out, the latter is more convenient. So we write

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

The problem now boils down to figuring out what A, B, k are. $\psi(x)$ must be a continuous function, and its first derivative must also be continuous. Otherwise, $\frac{d^2\psi}{dx^2}$ would be infinite and the kinetic energy would be infinite. This *condition* allows to write:

$$\begin{aligned} \psi(0) &= 0 \\ B\cos(0) &= 0 \quad \Rightarrow \quad B = 0 \end{aligned}$$

$$\begin{aligned} \psi(a) &= 0 \\ A\sin(ka) &= 0 \quad \Rightarrow \quad ka = n\pi \end{aligned}$$

where n is an integer.

Now have

$$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, 3, \ldots$$

There is still one unknown: A. To get it, we use the *normalization condition* of the wavefunction.

$$\begin{aligned} \int_0^a \psi^*(x)\psi(x)\,dx &= 1 \\ A^2\int_0^a \sin^2(n\pi x/a)\,dx &= 1 \end{aligned}$$

The integral can be evaluated by integration by parts or by looking up a table of integrals: it is $a/2$. This gives

$$A = \sqrt{2/a}$$

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2}\sin(n\pi x/a) \qquad n = 1, 2, 3, \ldots$$

Look up the $\ddot{\text{S}}$ equation: once we know ψ, we can get the energy by taking the second derivative of $\psi(x)$, and multiply it by $-\hbar^2/2m\psi(x)$. When we do that (recall $\hbar = h/2\pi$) we get

$$E \equiv E_n = \frac{h^2 n^2}{8ma^2} \qquad n = 1, 2, 3, \ldots$$

Now we can get *physical insight* into QM as applied to the PIB model system by

drawing $\psi_n(x)$ for $n = 1, 2, 3, \ldots$

drawing $(\psi_n(x))^2$ for $n = 1, 2, 3, \ldots$

looking at values of E_n, $(E_{n+1} - E_n)$ and (E_{n+1}/E_n), in the limits of small n and large n, and see what the physical implications are.

$$E_n = \frac{h^2 n^2}{8ma^2} = n^2\, E_1 \qquad n = 1, 2, 3, \ldots$$

- the **zero-point energy** (ZPE) = $E_1 > 0$
- E is **quantized** bc the particle is **confined**
- E_{n+1}/E_n goes to 1 when n gets large, <u>and</u> $n \nearrow$ when $T \nearrow$
- $(E_{n+1} - E_n)$ is $\propto 1/m$ and $\propto 1/a^2$

<u>**Correspondence principle**</u>: energy quantization becomes less apparent, and CM works better, as mass (m), size (a) and energy (n, or temperature T) get larger.

A thought experiment
(Gedankenexperiment)

- Suppose a free e^- has a very small energy

- We measure its position like this:

(a) suddenly create a box of length a at x_0;
(b) yes or no: is the e^- in the box?

- Suppose we do find the e^- in the box.

What can we conclude ? ? ?

1. position $= x_0 \pm a/2$: uncertainty $\Delta x = a/2$

2. the energy is now *at least* $E = h^2/8ma^2$

3. so the energy changed **as a result of measuring the position**, by at least $h^2/8ma^2$

4. the momentum must have changed, also, by at least some δp. Let's *estimate* δp with the classical formula:

$$\delta p \approx \sqrt{2mE} = \sqrt{2mh^2/8ma^2} = h/2a$$

5. The product $\Delta x \delta p \geq h/4$

Heisenberg arrived at a similar, but more rigorous, result known as **Heisenberg's principle**:

"If we measure x and p **simultaneously**, the product of the two uncertainties on those measurements, $\Delta x \Delta p$, must be greater than or equal to $h/4\pi$"

The qualitative conclusion of our thought experiment is that there is something about QM that's totally different from CM:

with the "simple" act of measuring the position (x) of a particle, we changed its energy (E), its momentum (p), its wavefunction ($\psi(x)$) — we changed pretty much everything.

If we try to measure position (x) more accurately, by using a smaller box (smaller a), we produce a bigger change in energy (E).

Measurements are **not** *simple after all !*

Non-interactive measurements are impossible: the observer and the observed are "intertwined".

The PIB model can account *qualitatively* for two aspects of chemical interactions:

- short-range repulsion
- covalent bonding

Short-range repulsion and the PIB model

Take the interaction potential $U(r)$ of two H atoms in the H_2 molecule at point A ($r = 0.75$ Å), and point B ($r = 0.50$ Å). Why does U increase <u>so much</u> from A to B? The electrostatic potential does not change that much:

- $V_{ee} \nearrow$ bc of 1 e^- pair getting closer
- $V_{nn} \nearrow$ bc of 1 pair of nuclei getting closer
- $V_{en} \searrow$ bc of 2 e^- nucleus pairs getting closer

According to the **covalent bond** model, e^- locate themselves preferentially *in between* the nuclei. That's like having two dipoles pointing at each other. So the net $(V_{ee} + V_{nn} + V_{en})$ should be *positive* (repulsive), but *fairly small.* Let's make a rough estimate.

Assume the e$^-$ are at 1/3 and 2/3 of the way between the two nuclei, and calculate the electrostatic interaction of the two dipoles in case B and case A. In a.u., $r = 0.945$ and $r = 1.417$, and

$$U_{B,elec.} \approx 1/0.945 + 1/0.315 - 2/0.630 = 1.058$$

$$U_{A,elec.} \approx 1/1.417 + 1/0.472 - 2/0.945 = 0.706$$

$$\Delta U_{elec.} \approx 0.35\, a.u. = 9.6\,\mathrm{eV}$$

Now consider the kinetic energy (next page).

We model a H_2 molecule with internuclear distance r as two e^- in a box of dimension $a = 2r$ in state $n = 1$. The difference in kinetic energy between B and A is then estimated to be, in a.u.,

$$\Delta(KE) \approx (4\pi^2/8)(1/1.89^2 - 1/2.834^2)$$

$$= 0.77\,\text{a.u.} = 21\,\text{eV}$$

This is twice as big as the change in electrostatic energy. What we conclude from this admittedly crude model is this:

"*The steep short-range repulsion is due mostly to a sharp increase in kinetic energy of the* e^- *when molecular size decreases.*"

Covalent bonding and the PIB model

We model two H atoms at infinite separation with two boxes of size $a = 2$ (a.u.). We know the equilibrium bond length of H_2 is 0.75 Å or 1.42 a.u. The appropriate box length to model H_2 is slightly less than twice that, say 2.5 a.u. A PIB has zero potential energy by definition, but not a zero kinetic energy. The difference in KE between H_2 and 2H estimated with this PIB model is

$$\Delta(KE) \approx [2(2\pi)^2/8]\,(1/2.5^2 - 1/2^2)$$

$$= -0.888\,a.u.$$

The electrostatic interaction can be modeled with dipoles as earlier: (a) it is zero for two infinitely separated H atoms; (b) for H_2 with e^- at 1/3 and 2/3 of the way between nuclei, we saw that $U_{A,elec.} \approx +0.706\,a.u.$

The net binding energy of H_2 is then

$0.888 - 0.706 = 0.182\,a.u.$ or 5 eV

The agreement with the true D_0 of H_2, 4.5 eV, is fortuitous. But it does show that the PIB model is not completely off. The *qualitative conclusion* that we can draw from this is that:

"*The main driving force for the formation of a covalent bond is the decrease in kinetic energy of e^- that results from sharing a single large box instead of having each e^- sit in its own small box.*"

Note.

The important role of *kinetic energy pressure* for understanding covalent bonding has been explained in great detail by Klaus Ruedenberg and Michael Schmidt, see J. Computational Chemistry 28 (2006) 391-410.

This 2006 paper builds upon an analysis of the chemical bond in H_2 and H_2^+ given earlier by K Ruedenberg, Reviews in Modern Physics 34 (1962) 326.

Chapter 20

the Hydrogen Atom

S̈ equation for H-like atoms

- $m_P \approx 1836 m_e$: assume the nucleus is fixed
- H atom: 1 electron and $Z = 1$
- Hydrogenlike atom: 1 electron, any $Z > 0$
- the e$^-$ moves in 3D: (x, y, z) or (r, θ, ϕ)
- e$^-$-nucleus potential $= -Z/r$.

Write $\hat{H} = \hat{T} - Z/r$, and solve

$$\hat{H}\psi = E\psi$$

- the wavefunctions depend on 3 QNs: n, ℓ, m_ℓ
- $\Rightarrow \ \psi_{n,\ell,m}(r, \theta, \phi)$
- $r \leftrightarrow n \quad ; \quad (\theta, \phi) \leftrightarrow \ell, m_\ell$
- energies E_n depend only on n **for H**

$$E_n = -C\mu Z^2/n^2$$

$C = \frac{1}{2}$ a.u. $= 13.606$ eV

Z: atomic *number*

n: 1, 2, 3, 4, …

and μ is a dimensionless **reduced mass**

$$\mu = \left(\frac{m_1 m_2}{m_1 + m_2}\right) \div m_e$$
$$= \frac{1836 \cdot 1}{1836 + 1} = 0.99946$$

$E_n \propto 1/n^2$ unlike the P.I.B. (see Fig. 20.2)

Wavefunctions ψ_{n,l,m_ℓ} are indexed by the QNs (n, l, m_ℓ):

$n = 1$: (1,0,0) = 1s

$n = 2$: (2,0,0) = 2s
(2,1,-1), (2,1,0), (2,1,1) = 2p

$n = 3$: (3,0,0) = 3s
(3,1,-1), (3,1,0), (3,1,1) = 3p
(3,2,-2), (3,2,-1), (3,2,0), (3,2,1), (3,2,2) = 3d
etc.

$n = 1, 2, 3, 4, \ldots$
$\ell = 0, 1, \ldots, (n-1)$
$m_\ell = -\ell, -\ell + 1, \ldots, \ell - 1, \ell$

$\ell =$ 0 (s), 1 (p), 2 (d), 3 (f), 4 (g), …

$$\psi_{n,\ell,m} = R_{n,\ell}(r) \times Y_{\ell,m}(\theta,\phi) \times N_{n,\ell,m}$$

$R_{n,\ell}(r)$: radial function

$Y_{\ell,m}(\theta,\phi)$: spherical harmonic, angular function

$N_{n,\ell,m}$: normalization constant

The wavefunctions of the H atom are normalized

$$\int |\psi_{n,\ell,m}(r,\theta,\phi)|^2 = 1$$

and mutually orthogonal

$$\int \psi^*_{n,\ell,m}\,\psi_{n',\ell',m'} = 0$$

because of $Y_{\ell,m}(\theta,\phi)$ when $n = n'$

because of $R_{n,\ell}(r)$ when $\ell = \ell'$ and $m = m'$

A wavefunction that depends on the coordinates of only one electron is called an **orbital**.

The wavefunctions of the H-like atom are **atomic orbitals (AO)**

Isovalue surfaces

To depict a function of 3 variables, $\psi_{n,\ell,m}(r,\theta,\phi)$:

- Take a specific AO $\psi_{n,\ell,m}$

- For that AO, take **every** point (r',θ',ϕ') in space that satisfies

$$|\psi_{n,\ell,m}(r',\theta',\phi')| = 0.01000000$$

- The set of all those (r',θ',ϕ') points makes a 2D surface (a shape) in 3D space: it is the *contour* of the AO for the value 0.01.

A isovalue *surface* projected onto a plane gives a *line*, a contour. See Fig. 20.7 for contours of 1s, 2p, and 3d AOs.

Exercise:

Sketch the shape of wavefunctions that have $(n, \ell) =\ (1,0),\ (2,0),\ (2,1),\ (3,1),\ (3,2)$

Exercise:

Make a sketch where you represent the energy on vertical axis and indicate the position of energy levels for all the H atom wavefunctions with $n \leq 4$. On that sketch, indicate the minimum energy we must supply to detach the e^- from the proton; also indicate the energy range for unbound states.

Exercise:

Reproduce Fig. 20.6 on page 454 and explain how the shape of the 1s, 2s, and 3s AOs are consistent with the fact that these orbitals are mutually orthogonal:

$$\int \psi^*_{1,0,0}\, \psi_{2,0,0} = 0$$

$$\int \psi^*_{1,0,0}\, \psi_{3,0,0} = 0$$

$$\int \psi^*_{2,0,0}\, \psi_{3,0,0} = 0$$

Exercise:

Sketch the shape of a $s - type$ and a $p - type$ function on the same graph, and use that to explain how

$$\int \psi^*_{2,0,0}\, \psi_{2,1,0} = 0$$

Same exercise, but this time with a $p - type$ and a $d - type$ function, to explain how

$$\int \psi^*_{3,1,0}\, \psi_{3,2,0} = 0$$

$$\int \psi^*_{3,1,0}\, \psi_{3,2,1} = 0$$

$\psi_{n,\ell,m}$ has ℓ angular nodes, $(n - \ell)$ radial nodes, and n nodes in total.

As $n \nearrow$, the number of nodes $\nearrow$, and
the energy $\nearrow$

$|\psi_{n,\ell,m}(r,\theta,\phi)|^2\ dV$: probability of finding the e^- inside volume dV around the point (r,θ,ϕ).

$$dV = dr \times r\sin\theta d\phi \times r d\theta$$

$[R_{n,\ell}(r)]^2$: probability density of e^--nucleus distances.

(See Fig. 20.10, page 459)

Comments

1. The H atom potential, $-1/r$, is highly symmetric (spherical symmetry). This is what causes the high degree of degeneracy among AO.

2. The H atom potential $\rightarrow -\infty$ when $r \rightarrow 0$. This is what causes the restrictions on the QNs $\ell < n$ and $|m_\ell| \leq \ell$

3. the spacing between energy levels E_n and E_{n+1} **decreases** as n increases (unlike the PIB) because, at higher energies, the e$^-$ is effectively in a bigger box.

4. The H atom is really a 4D system: x, y, z and time t. The **relativistic $\ddot{\text{S}}$ equation** (Dirac, 1929) gives 4 QNs: n, ℓ, m_ℓ and m_s

5. $m_s = -1/2$ ($\downarrow$, α), $+1/2$ ($\uparrow$, β): magnetic QN, or "electron spin"

6. in a magnetic field, atoms having a $m_s = -1/2$ e^- are deflected differently than atoms having a $m_s = +1/2$ e^- (Stern-Gerlach expt)

Shell Model of the Atom

Bohr's model, 1913: e^- can move around H^+ only on one of many possible *orbits*, $n = 1, 2, 3 \ldots$

QM, 1926: e^- described by *orbitals* ($n = 1, 2, 3 \ldots; \ell, m$).
Radial distribution function for 1s, 2s, 3s, … are like **thick, fuzzy** versions of Bohr's orbits.

See Fig. 20.12

Fig. 20.10 shows electronic shells.

Orbitals in order of most probable distances:

$1s < 2p < 2s < 3d < 3p < 3s < \dots$

The $2s$ is large where the $1s$ is small;

The $3s$ is large where the $1s$ and $2s$ are small;

The $3p$ is large where the $2p$ is small;

etc.

Helium Atom

$Z = 2$, two e$^-$. The hamiltonian has a part $\hat{H}_1$ that depends only on the coordinates of e$^-$ #1, a part $\hat{H}_2$ that depends only on the coordinates of e$^-$ #2, and a inter-electronic repulsion term $(1/r_{12})$ that depends on both e$^-$.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + 1/r_{12}$$

$$\hat{H}_1 = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - 2/r_1$$

It is *impossible* to solve *exactly* the S̈ equation with this hamiltonian!

Independent e^- approximation:

$$\hat{H} \approx \hat{h}_1 + \hat{h}_2$$

$$\hat{h}_1 = \hat{H}_1 + U_{1,eff}(x_1, y_1, z_1)$$

$$\hat{h}_2 = \hat{H}_2 + U_{2,eff}(x_2, y_2, z_2)$$

$U_{1,eff}$ is a fictitious potential that mimicks the effect of $1/r_{12}$. With this approximation, the solutions to the S̈ equation have the form

$$\psi = \phi_1(x_1, y_1, z_1)\, \phi_2(x_2, y_2, z_2)$$

$$E = E_1 + E_2$$

ϕ_1 and ϕ_2 are atomic orbitals (AO) and E_1 and E_2 are the orbital energies.

In particular, if

$$U_{eff}(x, y, z) = 0$$

ϕ_1 and ϕ_2, and E_1 and E_2, are *exactly* as for a hydrogenlike atom with $Z = 2$ (pages 448-451).

The independent e^- approximation is also called

orbital approximation, or,

one-electron approximation

It is the basis for the method

Linear Combination of Atomic Orbitals-Molecular Orbital (LCAO-MO)

for studying the electronic structure of atoms and molecules.

$1s(2)$: “$1s$ orbital of He$^+$ with the coordinates of electron 2”.

For the He *ground state*:

$$\begin{aligned}\psi(1,2) &= 1s(1)\,1s(2)\\[2ex] E &= E_1 + E_2 = 2\cdot 2^2\cdot(-13.606\,eV)\\[2ex] &= -108.8\,eV\end{aligned}$$

Neglecting $1/r_{12}$ is a rough approximation. Estimate the e-e repulsion energy V_{ee}: suppose one e$^-$ is *at* the nucleus and the other is described by a H-atom $1s$ function: then, the e-e potential energy is exactly equal to minus the e–proton potential energy of the H atom, that is, 27.2 eV (see pages 452-453). So $V_{ee} \approx 27.2$ eV.

With $V_{ee} \approx 27.2$ eV, we get an estimate for the He ground state energy

$$E \approx -108.8 + 27.2 = -81.6\,\mathrm{eV}$$

The most precise calculation on He gives

$$E = -79.01019\,\mathrm{eV}$$

A more accurate estimate of V_{ee} is:

$$V_{ee} \approx \int [1s(1)1s(2)]\,(1/r_{12})\,[1s(1)1s(2)]\,d\tau$$

$$= 34.0\,eV$$

Note that evaluating this integral is *not* easy at all. With $V_{ee} \approx 34.0$, our new energy estimate for He is

$$E \approx -108.8\,eV + 34.0\,eV$$

$$= -74.8\,eV$$

Curiously, this is not as close to the true value (-79.01019) as the earlier estimate (-81.6).

There is another way to estimate the ground state energy of He. Half of the time e$^-$# 1 is closer to the nucleus than e$^-$# 2: when that happens, e$^-$# 2 sees a net charge of +1. So, on average, e$^-$# 1 sees an effective **screened nuclear charge** $Z_{eff} \approx 1.5$. The same goes for e$^-$# 2: it sees a $Z_{eff} \approx 1.5$. To take the e-e repulsion into account, we replace $Z = 2$ by $Z_{eff} = 1.5$ in the hydrogenoid atom energy expression and get

$$E = E_1 + E_2 = 2 \cdot (1.5)^2 \cdot (-13.606)$$

$$= -61.2\,\mathrm{eV} > -79.0\,\mathrm{eV}$$

Since the true energy of He is −79.0 eV, the correct Z_{eff} must be $(79/(13.606 \times 2))^{1/2} = 1.70$.

The previous calculation tells us that the electrons in He see, on average, an effective **screened nuclear charge** of roughly 1.70. We explain that it is bigger than 1.50 with *electron correlation.* Electrons dynamically avoid each other. So when one e^- is on "one side of the He atom", there is a higher than 50% chance that the other e^- is on the "other side". That results in less screening and $Z_{eff} > 1.50$.

Let's now estimate the energy of the He atom in its first excited state, configuration $1\mathrm{s}^1 2\mathrm{s}^1$. To get V_{ee} we assume, as before, that the 1s e^- is *at* the nucleus. The other e^- is described by a $2s$ orbital. We get V_{ee} as before, as the negative of V_{eN} for a H atom in a 2s state: $2 \times (1/4) \times 13.6 = 6.8$ eV.

$$
\begin{aligned}
E(1s2s) &\approx E_{1s}(Z=2) + E_{2s}(Z=2) + V_{ee} \\
&\approx -54.4 + -54.4/4 + 6.8 \\
&= -61.2\,\mathrm{eV}
\end{aligned}
$$

The true energy of He(1s2s) is -59.2 eV.

Another way to estimate energy of He($1s^1 2s^1$):

Assign e^- #1 to the 1s AO: this e^- sees $Z_1 = 2$ and has $n_1 = 1$.

Then e^- #2 is in the 2s AO: it sees $Z_2 = 1$ and it has $n_2 = 2$.

The energy is then

$$\begin{aligned} E &\approx -13.6 \times (Z_1^2/n_1^2 + Z_2^2/n_2^2) \\ &\approx -13.6 \times (2^2/1^2 + 1^2/2^2) = -57.8\,\mathrm{eV} \end{aligned}$$

Compared to the true value, -59.2 eV, it is in error by 2%.

Variational Principle. If ϕ is an *approximation* to the true ground state wavefunction ψ of an hamiltonian $\hat{H}$, then

$$E[\phi] > E[\psi] = E_{exact}$$

$$E[\phi] = \int \phi^* \hat{H} \phi \, d\tau$$

$$E[\psi] = \int \psi^* \hat{H} \psi \, d\tau$$

Pauli Exclusion Principle

A Law of Nature, or,
another Postulate in QM

The wavefunction of a many e^- system must be antisymmetric, ie, it must change sign when we interchange two electrons

As a result …

…In an atom, no 2 e^- can have the same 4 quantum numbers n, ℓ, m_ℓ, m_s

Aufbau Principle

The ground-state electronic configuration of an atom is obtained by filling atomic orbitals (AOs) with up to two e$^-$ each (one with $m_s = +1/2$, the other with $m_s = -1/2$) to satisfy Pauli principle. The order in which orbitals get filled is

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p …

Examples:

C ($Z = 6$): $1s^2\ 2s^2\ 2p^2$

Fe ($Z = 26$): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Exceptions:

after the normal filling order, transfer one of the highest energy e$^-$ to a d subshell for these:

Cr, Ni, Cu

Nb, Mo, Ru, Rh, Pd, Ag

La, Pt, Au

Ce, Gd

oh! and make that two e$^-$ for Pd.

Z_{eff}: **effective nuclear charge** experienced by an e$^-$ in an AO.

Example, Li $1s^2\,2s^1$:

e$^-$ in the 1s AO feel a $Z_{eff} \approx 2.5$

e$^-$ in the 2s AO feels a $Z_{eff} \approx 1.0$

Once we have the electronic configuration of an atom, we associate a Z_{eff}

$$Z_{eff} = Z - s$$

to each AO. The **screening** s for an AO is calculated using **Slater's rules** (next page).

Slater's rules

1. group AOs like this:
   (1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) etc.

2. e^- in groups to the right do not shield the AO

3. e^- in the same group contribute 0.35 to s

4. other contributions to s:

   for d and f AOs:
   1.00 from e^- in groups to the left

   for s and p AOs:
   0.85 from e^- with QN $(n-1)$ and
   1.00 from e^- in groups further left

Going back to the Li $1s^2\,2s^1$ example:

For the 1s $s = 0.35$ $Z_{eff} \approx 3 - 0.35 = 2.65$

For the 2s $s = 0.85 \times 2 = 1.70$

$$Z_{eff} \approx 3 - 1.70 = 1.30$$

The Z_{eff} one gets with these rules are useful. They allow to estimate **electron detachment energies** (EDE) such as

$$Fe(\ldots 4s^2\, 3d^6) \longrightarrow Fe^+(\ldots 4s^1\, 3d^6)$$

$$Fe(\ldots 4s^2\, 3d^6) \longrightarrow Fe^+(\ldots 4s^2\, 3d^5)$$

$$\begin{aligned} s &= 0.35 + 14 \times 0.85 + 10 = 22.25 \\ Z_{eff} &= 26 - 22.25 = 3.75 \\ EDE &\approx 13.6 \times (3.75/4)^2 = 12.0\,\mathrm{eV} \end{aligned}$$

$$\begin{aligned} s &= 5 \times 0.35 + 18 = 19.75 \\ Z_{eff} &= 26 - 19.75 = 6.25 \\ EDE &\approx 13.6 \times (6.25/3)^2 = 59\,\mathrm{eV} \end{aligned}$$

These estimates are very rough, but good enough to predict that the g.s. of Fe^+ is $4s^1\, 3d^6$.

Another use of Slater's Z_{eff} is comparing the size of different AOs, for example:

Sc: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
Co: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
Rh: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^7$

Sc $4s$: $s = 18$, $Z_{eff} = 3.00$ and $n = 4$
Co $4s$: $s = 23.1$, $Z_{eff} = 3.90$ and $n = 4$
Rh $5s$: $s = 41.1$, $Z_{eff} = 3.90$ and $n = 5$

The Sc 4s AO is bigger than the Co 4s AO bc its Z_{eff} is smaller;

The Rh 5s AO is bigger than the Co 4s AO bc its n is bigger.

Ionization Energy (IE)

Electron Affinity (EA)

$$A_{(g)} \rightarrow A^{+}_{(g)} + e^{-} \qquad \Delta E = IE$$

$$A^{+}_{(g)} \rightarrow A^{2+}_{(g)} + e^{-} \qquad \Delta E = IE_2$$

$$A^{-}_{(g)} \rightarrow A(g) + e^{-} \qquad \Delta E = EA$$

IE>0 for all atoms

EA>0 for *most* atoms.

Mulliken's electronegativity χ, also called "electrons' chemical potential"

$$\chi = \frac{1}{2}(IE + EA)$$

The stronger an atom holds on to its electrons, the higher its IE;

The stronger an atom attracts electrons, the higher its EA;

χ: overall tendency of an atom A to attract electrons, no matter what its formal charge is (A, $A^{-\delta}$, or $A^{+\delta}$).

Absolute hardness

$$\eta = \frac{1}{2}(IE - EA)$$

η: overall tendency of an atom to stay neutral.

A large η usually indicates a stable chemical species, for ex., He, Ne, …, N_2, CH_4, …

Why? *A hard molecule can not easily give or take electrons from a reaction partner. That prevents certain types of chemical reactions.*

HSAB Principle (Pearson and Parr)

In Lewis acid-Lewis base reactions …

…hard acids react faster with hard bases, and make more stable products;

…soft acids react faster with soft bases, and make more stable products.

Roughly what is the absolute hardness of the H atom?

(a) 13.6 eV

(b) 10.2 eV

(c) 6.8 eV

(d) 3.4 eV

(e) 0.0 eV

Ans.: (c) 6.8 eV Expt: 6.43 eV

Molecular Electronic Structure

H_2^+

Exercise.

Make a sketch of H_2^+ with its e^- at $\vec{\mathbf{r}}$, its nuclei at $\vec{\mathbf{R}}_a$ and $\vec{\mathbf{R}}_b$, and distances r_a, r_b, and R.

Then, write the hamiltonian $\hat{H}$ for H_2^+ (use a.u. and cartesian coordinates)

H_2^+ is a bit like two protons and one e$^-$ inside a box of dimensions 4 × 2 × 2 a.u. The PIB model gives *rough* estimates of kinetic energies in the ground state ($n_x = n_y = n_z = 1$, see Eqn. 15.25)

$$K \approx (h^2/8m)\left(\frac{1}{4^2} + \frac{1}{2^2} + \frac{1}{2^2}\right) = (2.8/m) \text{ a.u.}$$

$m = 1$ for the e$^-$, $m = 1837$ for protons: we get

$$\begin{aligned}&K(\text{e}^-) = 76 \text{ eV} = 1.2 \times 10^{-17} \text{ J}\\&K(\text{proton}) = 0.04 \text{ eV} = 6.6 \times 10^{-21} \text{ J}\end{aligned}$$

We can estimate the speed of the e$^-$ and protons

$$v = (2K/m)^{1/2} = (5.6/m^2)^{1/2} = (2.4/m) \text{ a.u.}$$

For the e$^-$ $v \approx 2.4$ a.u. $= 0.018$ c

for the proton, $v \approx 0.0013$ a.u. $= 0.00001$ c

In molecules, protons move roughly

2000 times slower than electrons

Born-Oppenheimer Approximation

From the viewpoint of electrons, nuclei appear to be fixed

From the viewpoint of nuclei, electrons appear smeared out, like a cloud of electrons

electron's viewpoint:

$\star$ Fix the nuclei a distance R apart

$\star$ Solve the S̈ equation for electron(s) $\Rightarrow E$

$\star$ Repeat for several $R \Rightarrow E(R)$:
$E(R)$ is a **potential energy curve**

As $R \rightarrow \infty$ we get H^+ and H, the energy is

$E_{el} = -13.6\,\mathrm{eV}$ (electronic energy)

or

$E = 0$ (conventional)

At R, we *approximate* $\psi(\vec{\mathbf{r}})$ by a **LCAO**:

$$\psi(\vec{\mathbf{r}}; R) \;=\; \left(c_a e^{-r_a} + c_b e^{-r_b}\right)/\sqrt{\pi}$$

$e^{-r_a}/\sqrt{\pi}$ is a 1s AO centered around nucleus "a". We represent it by $1s_a(\vec{\mathbf{r}})$.

The e$^-$ density must be the same on both sides of the molecule, so

$$c_a^2 = c_b^2 \;\;;\;\; c_a = \pm c_b \quad \textit{by symmetry}$$

This gives only 2 possibilities

$$\psi_g \;=\; N_g\left[1s_a(\vec{\mathbf{r}}) + 1s_b(\vec{\mathbf{r}})\right]$$

$$\psi_u \;=\; N_u\left[1s_a(\vec{\mathbf{r}}) - 1s_b(\vec{\mathbf{r}})\right]$$

N_g, N_u: normalization factors

Define S (**overlap**), α and β:

$$S = S_{ab} = \int 1s_a(\vec{\mathbf{r}})^* \, 1s_b(\vec{\mathbf{r}}) \, d\vec{\mathbf{r}}$$

$$\alpha = H_{aa} = \int 1s_a(\vec{\mathbf{r}})^* \, \hat{H} \, 1s_a(\vec{\mathbf{r}}) \, d\vec{\mathbf{r}}$$

$$\beta = H_{ab} = \int 1s_a(\vec{\mathbf{r}})^* \, \hat{H} \, 1s_b(\vec{\mathbf{r}}) \, d\vec{\mathbf{r}}$$

Then

$$N_g = [2(1+S)]^{-1/2}$$

$$N_u = [2(1-S)]^{-1/2}$$

$$E_g = \alpha + \left(\frac{\beta - S\alpha}{1+S}\right)$$

$$E_u = \alpha - \left(\frac{\beta - S\alpha}{1-S}\right)$$

Which of these look like reasonable values (in eV) for the α and β integrals of the H_2^+ molecule?

(a) $\alpha = -20 \;\; ; \;\; \beta = +10$

(b) $\alpha = -20 \;\; ; \;\; \beta = -10$

(c) $\alpha = -10 \;\; ; \;\; \beta = -10$

(d) $\alpha = -10 \;\; ; \;\; \beta = -20$

(e) $\alpha = -20 \;\; ; \;\; \beta = -20$

Ans.: (b)

α : energy of an e$^-$ in a 1s AO in the presence of a second proton (must be < -13.6 eV)

β : energy of a fraction of e$^-$ ($\approx$ half an e$^-$) located in the region *between* the two nuclei

In general, the overlap S of two AO is a number between -1 and $+1$.
In our H_2^+ example, $0 < S < 1$.

When H_2^+ is near its equilibrium distance, 2.0 a.u., we have

$$\alpha \approx -25\,\mathrm{eV}$$

$$\beta \approx -18\,\mathrm{eV}$$

$$S \approx 0.46$$

$$E_g \approx -25 + \frac{-18 - 0.46(-25)}{1.46} = -29.5\,\text{eV}$$

$$E_u \approx -25 - \frac{-18 - 0.46(-25)}{0.54} = -13.0\,\text{eV}$$

For the g.s. of H_2^+ $\quad E_{el.} = -29.5\,\text{eV}$ and

$$\begin{aligned} E &= -29.5 + V_{nn} \\ &= -29.5 + (1/2.00)(27.2) = -15.9\,\text{eV} \end{aligned}$$

The dissociation energy of H_2^+ is

$$\approx -13.6 - (-15.9) = 2.3\,\text{eV}$$

The ionization energy of H_2^+ is

$$\approx 29.5\,\text{eV}$$

The excitation energy for H_2^+ is

$$\approx -13.0 - (-29.5) = 16.5\,\text{eV}$$

Energy diagram of H_2^+:

ϕ_g: bonding MO; “g” for “*gerade*” (even)

ϕ_u: antibonding MO; “u” for “*ungerade*” (odd)

- combining 2 AOs gave 2 MOs

- $\frac{1}{2}(E_g + E_u) - E_{1s} > 0 \quad ; \quad$ and the bigger S is, the larger it is …

- …in general: the average energy of the MOs obtained by mixing n AOs is higher than the average energy of the AOs.

- If $S = 0.46$: $N_g = 0.59$ and $N_u = 0.96$.
  The antibonding MO is more diffuse.

- ψ_g has 0 node, ψ_u has 1 node.

$$H_2^+(R = 2a_0) \Rightarrow H_2^{2+}(R = 2a_0) + e^- \quad \Delta E =?$$

Which of these is closest to ΔE in eV?

(a) 3

(b) 11

(c) 17

(d) 26

(e) 30

Ans.: (e) 30

Minimal Basis LCAO-MO

for H_2, He_2

- Construct ψ by mixing $1s_a(\vec{\mathbf{r}})$ and $1s_b(\vec{\mathbf{r}})$

- Ignore the $2s, 2p, 3s, 3p, 3d, \ldots$ AOs

- Using Slater determinants ensures that ψ is antisymmetric, ie, that it satisfies Pauli principle.

Lower MO, $1\sigma_g$: bonding

Upper MO, $1\sigma_u$: antibonding

H_2	$(1\sigma_g)^2$
He_2^+	$(1\sigma_g)^2 \ (1\sigma_u)^1$
He_2	$(1\sigma_g)^2 \ (1\sigma_u)^2$

bond order $\quad B = (N_b - N_a)/2$

Expt bond energy D_e in eV:

	H_2	He_2^+	He_2
B	1.0	0.5	0
D_e	4.75	2.5	0.0

Two problems with a minimal basis:

(1) Probability of $H_2 \leadsto H^- + H^+ \quad = 0.5$

In fact, it should be ≈ 0.063 at $R = R_e$

(2) Energy is inaccurate.

predicted $D_e(H_2) = 2.64\,\mathrm{eV}$

expt: $D_e(H_2) = 4.75\,\mathrm{eV}$

Make progressively better ψ by

- mixing 1s$_a$ and 1s$_b$; and 2s$_a$, 2s$_b$; and 2p$_{za}$, 2p$_{zb}$ …
- describing **electron correlation**, to get it right in **(1)**

Better $\psi_{el.}$ for H_2

- $1\sigma_g$ and $1\sigma_u$ are mixtures of 1s, 2s, 2p$_z$, 3s, 3p$_z$, 3d$_{z^2}$, 4s, … AOs

- If we mix $7 \times 2 = 14$ AOs $\Rightarrow$ 14 MOs: $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, …, $7\sigma_g$, $7\sigma_u$

- We can make $28 \times 27/2 = 378$ different Slater determinants

- ψ_{el}: apply the variational principle to get the best mixture of those 378

$\Rightarrow$ 1 ground-state and 377 excited states

Rules of AO mixing

AOs “a” and “b” mix to form MOs if:

- $|S_{ab}|$ is appreciable, $|S_{ab}| > 0.1$ roughly
- their energies are comparable,
  $|E_a - E_b| < 10$ eV roughly
- the larger $|S_{ab}|$ is, the more AOs mix
- the smaller $|E_a - E_b|$ is, the more AOs mix

When 2 AOs have
different symmetry: $S_{ab} = 0$

AO interactions in diatomics

Interactions of *d*-type AOs give:

$3d_{z^2}$: σ_g and σ_u
$3d_{xz}, 3d_{yz}$: π_g and π_u
$3d_{x^2-y^2}, 3d_{xy}$: δ_g and δ_u

MOs by mixing two AOs “a” and “b”

(1) small S_{ab}, small ΔE_{ab}

(2) big S_{ab}, small ΔE_{ab}

(3) big S_{ab}, big ΔE_{ab}

Exercise. Assume $E_a < E_b$ for AOs in every case. Suppose you start with N_a e$^-$ in AO "a" and N_b e$^-$ in AO "b" and you form MOs as in the 3 cases of the previous page.

How strong and how ionic will the bond be in the 15 cases described below?

a) $N_a = 1, N_b = 0$; all 3 cases

b) $N_a = 1, N_b = 1$; all 3 cases

c) $N_a = 2, N_b = 0$; all 3 cases

d) $N_a = 2, N_b = 1$; all 3 cases

e) $N_a = 2, N_b = 2$; all 3 cases

MO diagram for O_2

Energy ordering: $\cdots 1\pi_u\ 3\sigma_g \cdots$ for Li_2 to N_2

$\cdots 3\sigma_g\ 1\pi_u \cdots$ for O_2 to Ne_2

The bond orders

H_2	He_2	Li_2	Be_2	B_2
1	0	1	0	1
C_2	N_2	O_2	F_2	Ne_2
2	3	2	1	0

explain trends in

- bond lengths R_e (microwave spectra),
- bond strengths D_e (equilibrium constants),
- and bond stiffness ω_e (infrared spectra).

see Fig. 23.19

Lewis Structure Theory

A method to assign positions to e^- in molecules.

It gives *formal* atomic charges and bond orders, and an overall description of electron distribution and bonding.

Empirical observation: Rare gas atoms are chemically inert (stable) and have electronic configurations ending with either

- **2 e^-** : $1s^2$ (He)
- **8 e^-** : ns^2 np^6 (Ne, Ar)
- **18 e^-** : $(n\text{-}1)d^{10}$ ns^2 np^6 (Kr, Xe)
- **32 e^-** : $(n\text{-}2)f^{14}$ $(n\text{-}1)d^{10}$ ns^2 np^6 (Rn)

Basic Principles of Lewis Theory

1. Only the valence e^- of atoms rearrange themselves upon the formation of a molecule.

2. The e^- normally distribute themselves in a way that reproduces the configuration of a rare gas around each of the atom-in-molecule (AIM), with 0, 2, 8, 18, or 32 e^- around each AIM.

3. $+/-$ charge separation comes at an energy cost, therefore, e^- normally arrange themselves in a way that minimizes charges on AIMs.

For main group elements, put N dots around the symbol of an element to depict its N valence e$^-$:

Group I: H Na K Rb

Group II: Be Mg Ca

Group III-VII: Al Si P S Cl

Depending on how e$^-$ redistribute, we may have covalent, ionic, or polar bonds:

N_2

NaF

HCl

Molecules with more than 2 atoms

We start by determining which atoms are *central* and which ones are *terminal*.

Atoms of elements nearest Group IV are normally central atoms.

then . . .

1. V: number of valence e$^-$ in the molecule.
2. In steps 3 to 6, subtract from V every time e$^-$ are assigned a position in the molecule.
3. assume one or more central atom(s) and write a skeleton structure using single bonds only.
4. complete octets on terminal atoms.
5. complete octets on central atoms.
6. if a central atom lacks an octet, convert lone pairs on terminal atoms into bond pairs. That gives rise to *multiple bonds*.

Sometimes one can write many different Lewis structures for a molecule. Two criteria to decide which is "best":

(1) Minimize $\sum_j Q_j^2$, where Q_j is the formal charge on atom j.

$$Q_j = V_j - U_j - B_j$$

V_j is the valence. U_j is the number of unpaired e^-, and B_j the number of bonds, around atom j.

(2) For the same $\sum_j (Q_j)^2$, the best structure is the one with negative formal charges on the most electronegative elements.

Note: $\sum_j Q_j =$ true net charge on the molecule.

Exercise

Write 6 different Lewis structures for NOCl that satisfy the octet rule. Calculate the formal charges for each, and identify the best of those 6 Lewis structures.

Resonance

Sometimes one can write many different *and equally good* Lewis structures for a molecule. The best Lewis structure is then an "average" of those, called a **resonance hybrid**.

Exercise

Write 3 Lewis structures for SO_3 that are equivalent by symmetry, and depict the resonance hybrid.

Electron deficient species

An example of that is $BeCl_2$. You can write two Lewis structures.

One satisfies the octet rule, but has very bad formal charges Q_j.

The other has all $Q_j = 0$ but violates the octet rule: *it* is the better structure, with a electron deficient Be.

Electron rich species (expanded octet)

<u>Exercise</u>

Write two Lewis structures for $(\mathrm{SO}_4)^{2-}$: one with octets everywhere but a big $\sum_j (Q_j)^2$, and the other with a small $\sum_j (Q_j)^2$ but 12 e^- around the central S atom. The latter is the better Lewis structure.

Odd-electron species

When V is a odd number, it is impossible to satisfy the octet rule. We can use this method to write the Lewis structure:

(1) write a structure with 1 more (or 1 less) e^-

(2) remove (or add) 1 e^- so as to make the formal charges zero, or as small as possible.

<u>Exercise</u> Do that for NO

Bond orders

In Lewis theory, bond orders are the number of e^- pairs shared by two atoms. Write Lewis structures, and get the bond order, for HCl, Cl_2, N_2, CO_2.

Bonding in the water molecule

We will use H_2O to illustrate how different models work for a simple polyatomic molecule.

From experiment, we know that H_2O has:

- two equal O-H bond lengths, 0.9575 Å, and a bond angle $\theta = 104.51^\circ$
- electron removal energies of 13.0, 14.7, 18.6, and 38.0 eV.

(1) Lewis theory

It tells us that the connectivity is H—O—H, but says nothing about geometry or electron removal energies.

(2) Lewis + VSEPR

e^- pairs repel, they stay as far as possible from each other. This predicts $\theta = 109.5^\circ$

(3) Lewis + VSEPR + …

a lone pair occupies more space than a ligand.

That only tells us $\theta < 109.5^\circ$

(4) Valence Bond theory

Draw the valence AOs around each atom, and assign a geometry and e^- in AOs in such a way that *singly occupied AOs overlap as much as possible.* Simple VB theory predicts $\theta = 90^\circ$

(5) VB theory + electrostatics

OH bonds are polar and H atoms carry charges $+q$. The $H^{+q} \cdots H^{+q}$ electrostatic repulsion should force the angle to open up a bit, $\theta > 90°$.

If we know q and the strength of a OH bond, we can **estimate** θ.

Take $q = 0.46$ and $D_0(OH) = 4.8$ eV. As we go from $\theta = 90°$ to $\theta = 180°$, one OH bond is lost, so the energy increases by <u>4.8 eV</u>. But at the same time, the $H^{+q} \cdots H^{+q}$ repulsion energy goes down by <u>0.66 eV</u>:

$$\begin{aligned} \Delta U_{rep} &= (0.46)^2 \cdot 27.211 \cdot (1/2.559 - 1/3.619) \\ &= 0.66\,\text{eV} \end{aligned}$$

The two *opposing* effects (OH bond loss, and decrease in coulombic repulsion) tell us the equilibrium angle θ will be somewhere between 90° and 180°, and the relative magnitude of these two effects (4.8 eV vs 0.66 eV) suggest a θ of *roughly*

$$\begin{aligned}\theta &\approx 90 + \left(\frac{0.66}{4.8 + 0.66}\right)(180 - 90) \\ &= 101^\circ\end{aligned}$$

(6) Qualitative Molecular Orbital Theory

For small polyatomic molecules we can construct a MO energy diagram, like we do for diatomic molecules, by putting the AO energy levels of the **central atom** on one side, the AO energy levels of the **peripheral atoms** on the other side, and the resulting MO energy levels in the middle.

We need to assume a geometry in order to estimate AO overlaps and get reasonable MO energies. For H_2O, we assume θ between 90 and 120 degrees and these AO energies (eV): -13.6 for H(1s), -13.6 (the IE of O) for O(2p), and -32.4 for O(2s).

The MO diagram below predicts H_2O electron removal energies (roughly 14, 15, 17, and 33 eV) which are close to the observed ones (13.0, 14.7, 18.6, and 38.0 eV).

(6) Qualitative MO Theory (continued)

H_2O has two identical OH bonds. But the two corresponding MO energies are *different*, -15 and -17 eV. There is no contradiction there. Each OH bond is made of contributions from two MOs. Conversely, each MO is delocalized over the two OH bonds. When an e^- is removed from one of the bonding MOs, both OH bonds are weakened.

Same goes for the lone pairs. They are identical. However, the two MOs that describe them (-14 eV and -33 eV) are different, and each of those two MOs contribute to both lone pairs.

In general, bonds and lone pairs have a definite position in space but do not have (or, do not always have) a definite energy. MOs are delocalized but have a definite energy.

All that is related to Heisenberg's principle: if you know the position "(x, y, z)" of an e^- very accurately, you know very little about its momentum "(p_x, p_y, p_z)" and energy. You can define the position of e^- (bonds, lone pairs, etc.), or the energy of e^- (orbitals, electronic states), but you can not define both of those things simultaneously.

Symmetry

Why study symmetry?

- often, $\int \psi_1 \hat{O} \psi_2 \, d\tau = 0$ *by symmetry*

  $\Rightarrow$ spectra (IR, Raman, UV-vis, ...),
  overlap and bonding

- symmetric molecules are simpler:
  atoms $\Rightarrow$ small or symmetric molecules $\Rightarrow$ ...

- big molecules contain small symmetric groups
  –CH_2, –CH_3, phenyl, ...

- symmetry arises naturally because what's good for one C atom is good for all C atoms
  $\Rightarrow$ C_{60}; also Ar_{13}, fcc crystals, ...

Symmetry operation: a geometric operation that moves every point $\vec{\mathbf{r}}$ of 3D space to a new point $\vec{\mathbf{r}}\,'$, but leaves every nucleus unmoved *or* interchanges its position with that of an identical nucleus.

Symmetry element: a point, line, or plane that does not move under a given symmetry operation.

Examples

1: **ethylene**, C_2H_4: E, i, σ (3), C_2 (3)

The 8 sym. operations of C_2H_4 divide space into 8 sym. equivalent portions:

the electron density $\rho = |\psi|^2$ is identical at each point that is equivalent by symmetry to a given point $\vec{\mathbf{r}}_1$.

$$\rho(\vec{\mathbf{r}}_j) \;=\; \rho(\vec{\mathbf{r}}_1) \qquad\qquad j = 1, 8$$

Integrands of QM integrals:

$$\psi(\vec{\mathbf{r}}_j)\,\hat{O}\,\psi(\vec{\mathbf{r}}_j) \;=\; \pm\,\psi(\vec{\mathbf{r}}_1)\,\hat{O}\,\psi(\vec{\mathbf{r}}_1) \qquad j = 1, 8$$

The integral is *exactly zero* for certain *combinations of symmetry and integrand.*

\# 2: **staggered ethane**, C_2H_6: C_3, S_6, …

S_n: rotation by $2\pi/n$ followed by reflection across a plane perpendicular to the rotation axis.

The product of 2 sym. operations of a molecule is always a sym. operation of that molecule.

Successive applications of symmetry operations are (generally) non-commutative:

$$a_i \, a_j \neq a_j \, a_i$$

σ_h: reflection through a plane ⊥ to the main rotation axis C$_n$

σ_v: reflection through a plane that contains the main rotation axis C$_n$

σ_d: like σ_v except the plane of σ_d contains fewer atoms.

Notes about S$_n$:

S_1 is a σ ; $S_2 = i$

$(S_n)^2, (S_n)^4, \ldots$ are $C_n^2, C_n^4 \ldots$

Ex.: $S_8 \rightarrow S_8, (S_8)^3, (S_8)^5, (S_8)^7$ (and pure rotations)

The set of all sym. operations “a_j” of a finite object constitutes a **symmetry point group** “G”.

1. multiplication law:
   $\forall\, a_j, a_i \in G : \; a_j \cdot a_i = a_k \in G$

2. associativity:
   $\forall\, a_i, a_j, a_k : (a_i \cdot a_j) \cdot a_k = a_i \cdot (a_j \cdot a_k)$

3. identity element:
   $\exists\, a_1 \in G \,|\, \forall\, a_j : \; a_1 \cdot a_j = a_j \cdot a_1 = a_j$

4. inverse:
   $\forall\, a_j \, \exists\, a_k = (a_j)^{-1} \,|\, a_j \cdot a_k = a_k \cdot a_j = a_1$

$\forall$: for every $\exists$: there is a $\in$: in $|$: such that

Symmetry Point Groups

of Molecules

Follow the Flow Chart of Fig. 28.2 and show that

CH_4: T_d ; CH_3Cl: C_{3v} ; CH_2Cl_2: C_{2v}

eclipsed C_2H_6: D_{3h} ; staggered C_2H_6: D_{3d}

3 isomers of $C_2H_2Cl_2$: C_{2v}, C_{2v}, C_{2h}

3 isomers of $C_6H_4Cl_2$: C_{2v}, C_{2v}, D_{2h}

CO: $C_{\infty v}$; CO_2: $D_{\infty h}$

octahedron: O_h

distorted octahedra: D_{4h}, D_{2h}, D_{3d}, C_{3v}, ...

Molecules with **nonzero dipole moments** must belong to a C_s, C_n (including C_1), or C_{nv} group.

A molecule with **<u>any</u>** S_n sym. operation ($\mathrm{S}_1 = \sigma$, $\mathrm{S}_2 = i$, or other S_n) **can not be optically active**

A n-atom molecule has $(3n-6)$ vibrational modes of motion: each one of those has the symmetry properties of one of the **irreducible representations** of the point group (appendix C)

Spectroscopy: some optical transitions between energy levels are *forbidden by symmetry*

Reactivity: some reactions are *forbidden* on account of *orbital symmetry*

Characters and Irreducible Representations (“irreps”)

The sym. operations of a molecule leave the nuclear framework unchanged.

But some things, such as *velocity vectors* and *AOs*, may change under sym. operations.

The irreps and characters of a point group (Appendix C) give us the different ways in which those things can change.

Atoms' velocities in H_2O and the C_{2v} irreps

Arrows represent the x, y, z velocity components of the H_2O molecule.

Γ_{red}: Effect of C_{2v} sym. operations on v_x, v_y, v_z.

	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	3	-1	$+1$	$+1$

Γ_{red} is a sum of 3 irreps: take the scalar product of Γ_{red} with each of the irrep …

$$A_1 : \ (3,-1,1,1)\cdot(1,1,1,1)\div 4 = 1$$

$$A_2 : \ (3,-1,1,1)\cdot(1,1,-1,-1)\div 4 = 0$$

$$B_1 : \ (3,-1,1,1)\cdot(1,-1,1,-1)\div 4 = 1$$

$$B_2 : \ (3,-1,1,1)\cdot(1,-1,-1,1)\div 4 = 1$$

$$\Gamma_{red} = A_1 + B_1 + B_2$$

Properties of irreps (see section 27.4, 27.5, and Appendix C)

- Let the no. of sym. operations = n.
  n is called the *order of the group*.
- There are n irreps in a group.
- Each irrep is like a vector with n components, one for each sym. operation.
- The irreps are orthonormal.
- Every Γ_{red} can be decomposed as a sum of irreps.

Γ: a reducible symmetry representation of G

Γ_i: i'th character of Γ

χ^j: one of the irreps of G

χ^j_i: the i'th character of irrep j

$$\Gamma = c_j \, \chi^j$$

$$c_j = \frac{1}{n} \sum_i \Gamma_i \cdot \chi^j_i$$

Allowed Transitions in

Infrared and Raman Spectra

- CH_2O , C_{2v}

- C_2H_4 , D_{2h}
- C_2H_4 : CC stretch
- C_2H_4 : CH stretches
- C_2H_4 : out-of-plane deformations

- NH_3 , C_{3v}

Γ_{red} for nuclear motions

1. identify the point group
2. apply the sym. operations, one at a time
3. Get Γ_{red} : for each **unmoved** atom, count
    - $+3$ for E
    - -3 for i
    - $+1$ for a σ
    - -1 for C_2 ; 0 for C_3 ; $+1$ for C_4
4. take scalar products of Γ_{red} with irreps
5. look up the character table
    - x, y, z: (a) translation of molecule, and
      (b) IR allowed
    - R_x, R_y, R_z: rotations of the molecule
    - xy, xz, … z^2: Raman allowed

How do we get the correct “count” for each unmoved atom (+3 for E, −3 for i, +1 for a σ, etc.) for a given symmetry operation?

Here’s the general method (see next page)

(1) Imagine an atom positioned somewhere on the symmetry element (plane, line, or point) associated with the symmetry operation

(2) Imagine 3 unit-length vectors at right angles, $\vec{x}$, $\vec{y}$, $\vec{z}$, centered on that atom

(3) Apply the symmetry operation to this rigid set of 3 vectors: after the symmetry operation, you get 3 new vectors $\vec{x}'$, $\vec{y}'$, and $\vec{z}'$.

(4) Calculate the sum of the 3 scalar products:

$$c = \vec{x} \cdot \vec{x}' + \vec{y} \cdot \vec{y}' + \vec{z} \cdot \vec{z}'$$

The result, c, is the count you must use for that symmetry operation ($c = 3$ for the E operation, $c = -1$ for a mirror plane operation, etc.)

Symmetry-Adapted Linear Combinations (SALC) of Atomic Orbitals

- H_2O (C_{2v})
- NH_3 (C_{3v})
- HCN ($C_{\infty v} \rightarrow C_{4v}$)
- the π MOs of pyrazine (D_{2h})

1. find the point group
2. divide molecule into “central atom” + “the rest”
3. divide AOs into similar groups
   and get Γ_{red} for each of those groups
4. Decompose each Γ_{red} into irreps
5. Mix AOs that satisfy 3 conditions:
   - are in the same irrep
   - are in close proximity (overlap)
   - have similar energies