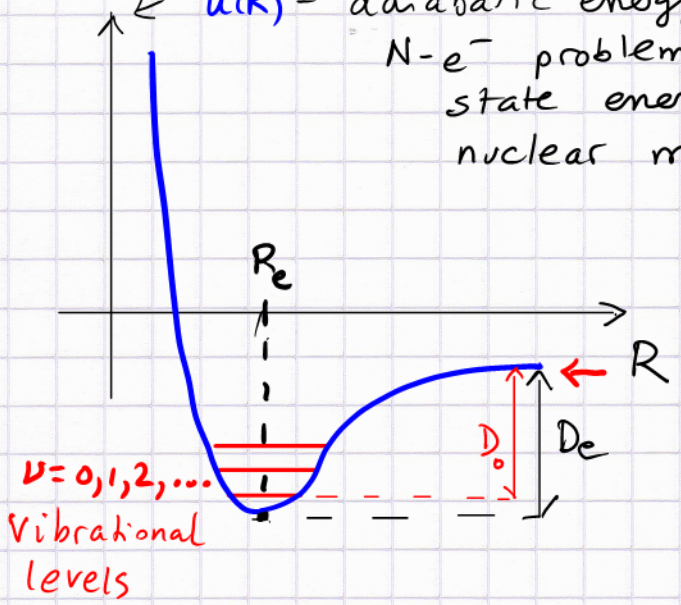
Potentials for atom-atom low-energy scattering

From quantum chem on diatomic molecules (eg. I. Levine: Q.C. textbook)

$U(R)$ = adiabatic energy curve from solving N-e^- problem @ fixed R + showing ground state energy → potential energy for nuclear motion (Born-Oppenheimer Appr.)



$U(R)$ includes nucleus-nucleus repulsion.

asymptotic energy reference

$D_e \equiv$ equilibrium dissociation energy $= U(\infty) - U(R_e)$

$D_0 \equiv D_e + \frac{1}{2}\hbar\omega$

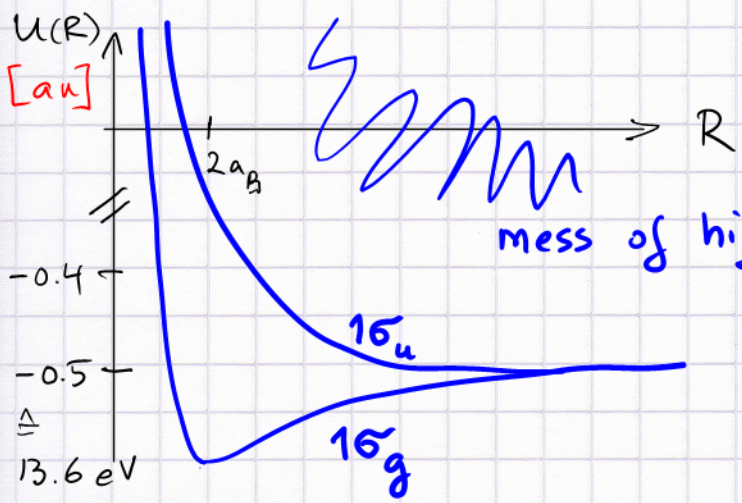
ground vibrational state dissociation energy

Idea: measure all (?) vibrational levels $\nu = 0, 1, \ldots, \nu_{max}$

→ deduce potential shape (Rydberg-Klein-Rees method)

problem: 1) uniqueness? 2) $U(R)$ outside the region of $|\psi_\nu(R)|^2$?

Reminder: nomenclature (H_2^+ molecule, ($pp\,e^-$) @ distance R)



mess of higher $n\sigma$, $n\pi$ which go over into H (n=2) levels ($U(\infty) = -.125$ au) → 27.1 eV

σ_u vs σ_g ?

≈ symmetric + antisymmetric linear combo of H(1s) orbitals on each proton

bonding vs antibonding

LCAO method

Classification of levels

atoms: (n, ℓ, m)

1) diatomic = axial symmetry survives!

2) principal number counting → ? from asymptotic $R \to \infty$ limit?
NO: new numbering scheme!

3) molecular orbitals (2 centre SE solutions)

separated atom	united atom (He^+ in H_2^+ case)	molecular symmetry
σ_g 1s	1s σ_g	$1\sigma_g$
σ_u^* 1s	2p σ_u^*	$1\sigma_u$
σ_g 2s	2s σ_g	$2\sigma_g$
σ_u^* 2s	3p σ_u^*	$2\sigma_u$
π_u 2p	2p π_u	$1\pi_u$
σ_g 2p	3s σ_g	$3\sigma_g$
π_g^* 2p	3d π_g^*	$1\pi_g$
σ_u^* 2p	4p σ_u^*	$3\sigma_u$

$*$ ⇒ antibonding
there is a nodal plane perpendicular to diatomic axis
⇒ low density between nuclei
→ high Pot. En.

MO labeling: use L-R nuclear parity (gerade / ungerade)
S (even) AS (odd)

use correlation sep./united atoms to understand:

$n_1 s$ / $n_2 s$ → σ states $m_1 = 0$ & $m_2 = 0$ ⇒ σ

$n_1 p$ / $n_2 p$ → σ when UA ⇒ np or ns $m_1 = 0$ & $m_2 = 0$
π when UA ⇒ np or nd $m_1/m_2 = 0/1$, $1/0$

σ, π, δ labels $m = 0, 1, 2, \ldots$ for MO

AO (m_1/m_2) → $m = m_1 + m_2$ combinations (e.g.: $2p_0 + 2p_1$)

NB: instead of $2p_0, 2p_1, 2p_{-1}$ often $\underbrace{2p_{1/-1}}_{} = 2p_x \pm i\,2p_y$
$2p_x, 2p_y, 2p_z = 2p_0$

$$Li_2 \rightarrow Li\,(1s^2 2s) + Li\,(1s^2 2s)$$

Li ($1s^2$) cores remain unaffected by bonding process
(very localized near nuclei)

$\hookrightarrow$ MOs : $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 \underbrace{(\sigma_g 2s)^2}_{\text{two net bonding orbitals}}$

(situation is trickier for $R \to 0$)

$^1\Sigma_g^+$ $\quad D_e = 1.07$ eV $\quad R_e = 2.67$ Å $\quad \tilde{\nu}_e = 351.4\ cm^{-1}$

what does this denote ?

1) we have a many e^- system (unlike H_2^+)

$\hat{L}_z = \sum_{i=1}^{N} \hat{L}_{i,z}$ is conserved (axial symmetry)

$\Lambda = |M_L|$ characterizes

Λ	0	1	2	3	4
label	Σ	Π	Δ	Φ	Γ
instead of	σ	π	δ	in H_2^+	

2) Total <u>electron</u> spin (by addition) $\rightarrow S$

use spin multiplicity $2S+1$ as a left superscript

spin singlet : $S = 0$ $\therefore$ $2S+1 = 1$ $\rightarrow$ the electron spins are paired up!

Note : the two valence e^- spins can also be added to $S = 1$,
$M_S = 1, 0, -1$

in this case the spatial symmetry of the coordinate space WF is AS

$\therefore$ higher energy (spin triplet $^3\Sigma$)

3) The + (or −) right superscript

refers to a spatial symmetry in the x-z plane
(z = internuclear axis) above/below z-axis

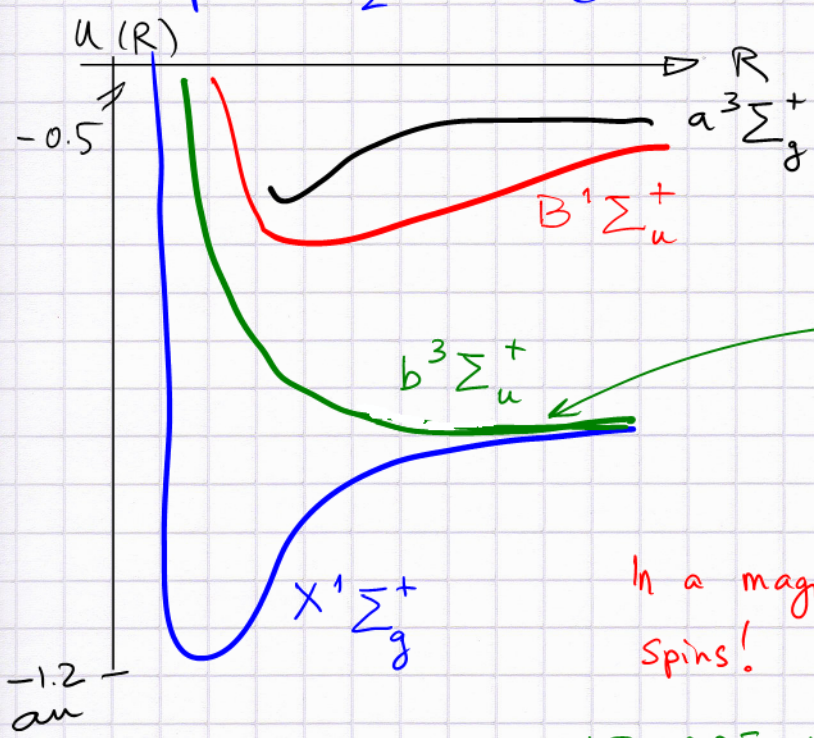
4) gerade / ungerade : works for homonuclear diatomics only!

5) spectroscopic conventions: ground state of molecule → put X

before term designation, excited state of same spin multiplicity → put A, B, C, ... before term

excited terms for other multiplicity: a, b, c, ...
(some exceptions are possible, e.g., C_2, N_2)

Example: H_2 molecule



a shallow well → NO VIB. BOUND STATES in H_2

However, in alkali-alkali systems this well does support bound states

In a magnetic trap the atoms have aligned spins! (Zeeman levels → quantization axis is given!)

⇒ WE ARE INTERESTED MOSTLY IN $^3\Sigma_u^+$!

Gribakin + Flambaum: $^3\Sigma_u$ potential characteristics
(PRA 48, 546)

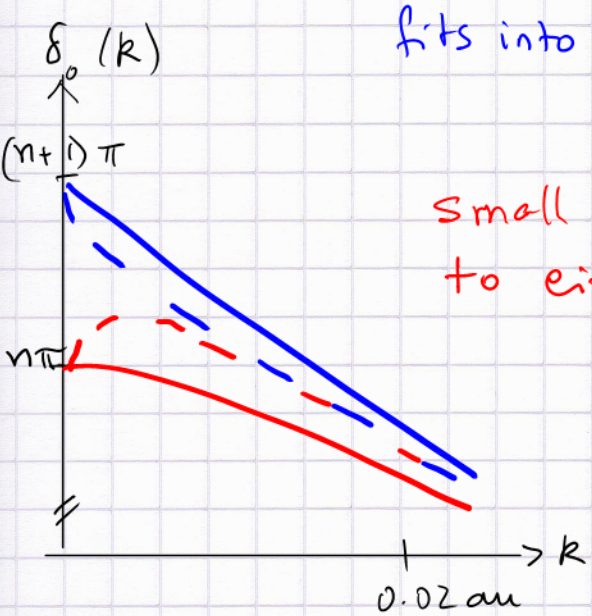
	U_{min} (au)	R_{min} (a_B)	N_{vib}	m_{atom}
H_2	-2×10^{-5}	7.9	0	1.836×10^3
Cs_2	-1.3×10^{-3}	12	50	2.422×10^5

deeper wider well + bigger $\mu = \frac{m_{atom}}{2}$ → !

G.+F. $\Rightarrow$ $\delta_0 = -ak$ $\sigma = 4\pi a^2$ at low T

$H_2\,(^3\Sigma_u)$ $a > 0$ of the order of molecular size (repulsive, even though vdW pot'l is attractive) [short-range "exchange" repulsion dominates]

$Cs_2\,(^3\Sigma_u) \longrightarrow$ whether $a < 0$ (attractive) or $a > 0$ (repulsive) depends crucially on how the last bound vib-level fits into the potential well



small changes in the potential can lead to either scattering phenomenon

$\left.\begin{array}{l} a > 0 \\ a < 0 \end{array}\right\}$ + large (lots of scattering)

attractive + large $\Rightarrow$ BEC candidate

large $a > 0$ $\Rightarrow$ no BEC, but strong scattering still implies interesting collective effects in a dense cloud!

G + F do : 1) motivation for a Cs-Cs potential

2) WKB based scattering length formula

(2) could be replaced by an accurate solution of the SE

(1) could be improved by more accurate fits to experimental spectroscopic information (RKR method to invert vibr. levels $\rightarrow U(R)$).
↳ Rydberg-Klein-Rees

In fact, photoassociation spectroscopy can measure nodes of high-lying rotational levels and "measure" $a > 0$ ("node") from extrapolation