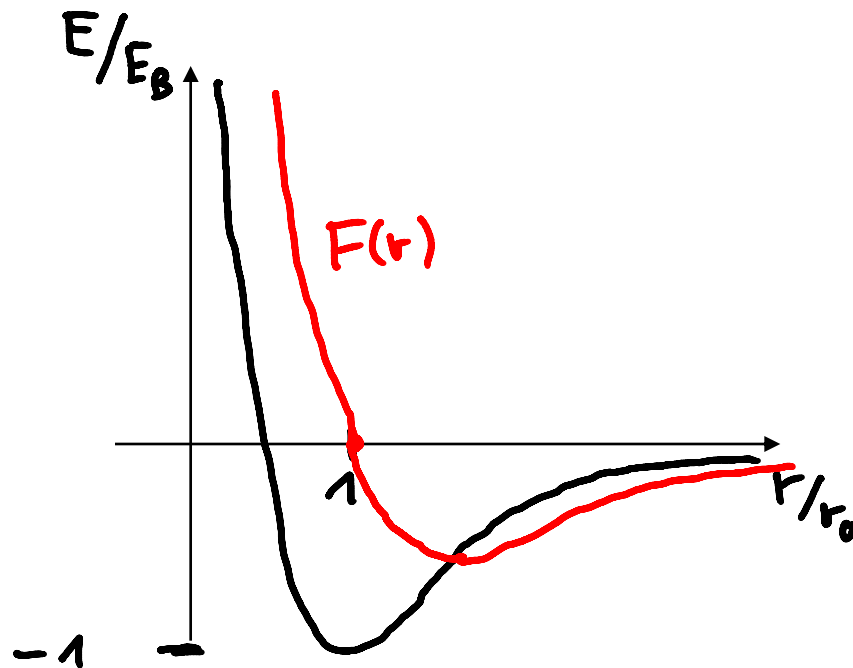


Chapter 01

Atomic interactions and forces

Typical shape of atomic interaction potentials



r_0 equilibrium distance

E_B binding energy

$$F(r) = - \frac{dE}{dr}$$

Quantum Mechanics

$$H_r \psi = E_r \psi$$

Calculate E for different r , determine force
as numerical derivative

Force in molecules

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Forces in Molecules

R. P. FEYNMAN

Massachusetts Institute of Technology, Cambridge, Massachusetts

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Formulas have been developed to calculate the forces in a molecular system directly, rather than indirectly through the agency of energy. This permits an independent calculation of the slope of the curves of energy *vs.* position of the nuclei, and may thus increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.

$$\bar{U} = \int \psi^* H \psi d\tau$$

$$1) F_{\lambda} = - \frac{d\bar{U}}{d\lambda}$$

Force defined as

$$2) F_{\lambda} = - \int \psi^* \frac{dH}{d\lambda} \psi d\tau$$

Hellman - Feynman theorem $1) \hat{=} 2)$

Derivation of the Hellmann-Feynman-theorem

$$H\psi = U\psi \quad H\psi^* = U\psi^* \quad \int \psi\psi^* = 1 \quad \left| \begin{array}{l} H \text{ is self-adjoint operator} \\ \int \psi^* H \frac{d\psi}{d\lambda} d\tau = \int \frac{\partial \psi}{\partial \lambda} H \psi^* d\tau \end{array} \right.$$

$$\frac{dU}{d\lambda} = \int \psi^* \frac{dH}{d\lambda} \psi d\tau + \int \frac{d\psi^*}{d\lambda} H \psi d\tau + \int \psi^* H \frac{d\psi}{d\lambda} d\tau$$

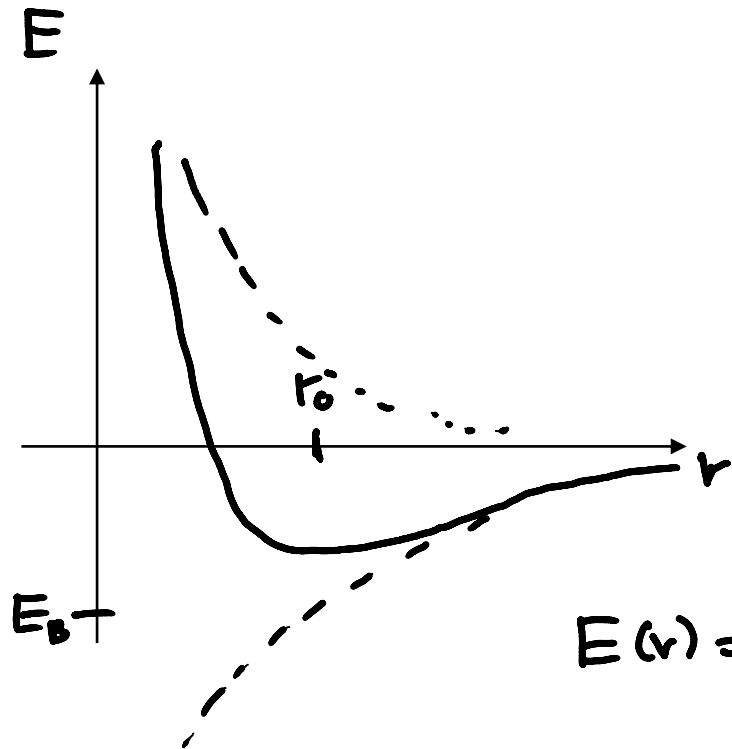
$$= \int \psi^* \frac{dH}{d\lambda} \psi d\tau + U \int \frac{d\psi^*}{d\lambda} \psi d\tau + U \int \frac{d\psi}{d\lambda} \psi^* d\tau$$

$$= \underbrace{\int \psi^* \frac{dH}{d\lambda} \psi d\tau}_{=0} + U \underbrace{\frac{d}{d\lambda} \int \psi^* \psi d\tau}_{=1}$$

$$\text{If } H = T + V \\ \frac{dH}{d\lambda} = \frac{dV}{d\lambda}$$

$$F_\lambda = - \int \psi\psi^* \frac{dV}{d\lambda} d\tau$$

Lennard-Jones potential



Attractive potential
van der Waals attraction

$$E_{\text{attr}} = -\frac{A}{r^6}$$

Need repulsive interaction

$$E_{\text{rep}} = \frac{B}{r^{12}}$$

$$E(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

$$r_0 = \left(\frac{2B}{A}\right)^{1/6}$$

$$E_B = \frac{A^2}{4B}$$

Van der Waals interactions – dipole interactions

$$\begin{array}{c} \mu \\ \nearrow \searrow \\ \text{---} r \text{---} \bullet \text{---} Q \end{array} - \frac{Q \mu \cos \Theta}{4\pi\epsilon_0 r^2} \qquad \begin{array}{c} Q \qquad \qquad \qquad \alpha \\ \bullet \text{---} r \text{---} \bullet \end{array} - \frac{Q^2 \alpha}{2(4\pi\epsilon_0) r^4}$$

$$\begin{array}{c} \mu \\ \nearrow \searrow \\ \text{---} r \text{---} \bullet \text{---} Q \end{array} - \frac{Q^2 \mu^2}{6(4\pi\epsilon_0) kT r^4} \qquad \begin{array}{c} \mu \qquad \qquad \qquad \alpha \\ \nearrow \searrow \qquad \qquad \bullet \end{array} - \frac{\mu^2 \alpha}{(4\pi\epsilon_0)^2 r^6}$$

$$\begin{array}{c} \mu \qquad \qquad \qquad \mu \\ \nearrow \searrow \qquad \qquad \nearrow \searrow \\ \text{---} r \text{---} \end{array} - \frac{\mu_1 \mu_2}{3(4\pi\epsilon_0)^2 kT r^6} \qquad \begin{array}{c} \alpha \qquad \qquad \qquad \alpha \\ \bullet \text{---} r \text{---} \bullet \end{array} - \frac{3}{4} \frac{h\nu \alpha^2}{(4\pi\epsilon_0)^2 r^6}$$

Van der Waals forces – dispersion forces

Dipole forces arise from correlation of quantum-mechanical charge fluctuations.

Over-simplified derivation from Bohr's model of the atom



Bohr's radius $a_0 = \frac{e^2}{2(4\pi\epsilon_0)h\nu}$ $h\nu = 2,2 \times 10^{-18} \text{ J} = 13,6 \text{ eV}$

No permanent dipole, but instantaneous $\mu = a_0 \cdot e$

Interaction energy $E(r) = - \frac{\mu^2 L_0}{(4\pi\epsilon_0)^2 r^6}$

and $L_0 = 4\pi\epsilon_0 a_0^3$

$E(r) = - \frac{2L_0^2 h\nu}{(4\pi\epsilon_0)^2 r^6}$

QM: $E(r) = - \frac{3}{4} \frac{L_0^2 h\nu}{(4\pi\epsilon_0)^2 r^6}$

Rough estimate of strength for van der Waals interactions

$$a_0^3 = \frac{\alpha_0}{4\pi\epsilon_0} \approx 1,5 \times 10^{-30} \text{ m}^3 \quad I = 2 \times 10^{-8} \text{ J} \quad r = 0,3 \text{ nm}$$

atoms in contact

$$E(r) = -4,6 \times 10^{-21} \text{ J} \approx 1 k_B T @ 300 \text{ K}$$

Quantum-mechanical derivation:

① Expand Coulomb interaction of electron distribution into powers of $1/r$

② Perturbation theory

1 st order	$\Delta E = 0$
2 nd order	$\Delta E = -\frac{3}{2} \frac{\alpha_{01} \alpha_{02}}{(4\pi\epsilon_0)^2 r^6} \frac{I_1 I_2}{I_1 + I_2}$

Van der Waals forces – all contributions

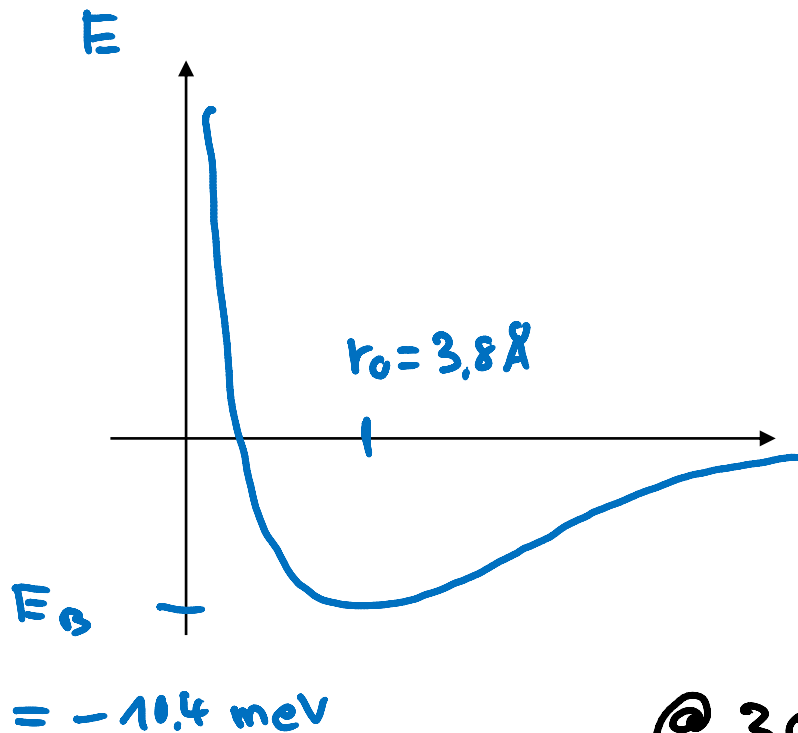
$$U_{vdW} = -\frac{1}{(4\pi\epsilon_0)^2 r^6} \left[\left(u_1^2 \alpha_{02} + u_2^2 \alpha_{01} \right) + \frac{u_1^2 u_2^2}{3kT} + \frac{3\alpha_{01} \alpha_{02} h \nu_1 \nu_2}{2(\nu_1 + \nu_2)} \right]$$

Debye energy
polarizable,
permanent
dipoles

Keesom
energy
permanent
dipoles

London energy
quantum
fluctuations

Lennard-Jones potential for an Ar₂ molecule



$$A = 2r_0^6 E_B = 63 \text{ \AA}^6 \text{ eV}$$

$$B = r_0^{12} E_B = 9.4 \times 10^4 \text{ \AA}^{12} \text{ eV}$$

$$E(r_0) = -\frac{2r_0^6 E_B}{r_0^6} + \frac{r_0^{12} E_B}{r_0^{12}} = -E_B$$

@ 300K $k_B T = 26 \text{ meV} > |E_B|$

binding only for $T < 100 \text{ K}$