Introduction to electronic structure theory

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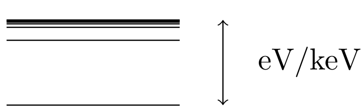
Energy scales

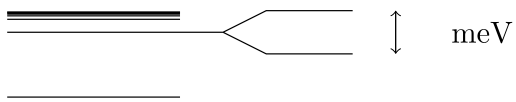
- Energy level structure: $\hat{H}\,|\psi_\alpha\rangle = E_\alpha\,|\psi_\alpha\rangle$



$$\text{for H:}\quad \alpha : \begin{cases} n = 1, 2, 3, \dots \\ \ell = 0, 1, 2, 3, \dots, n-1 \\ m_\ell = -\ell, -\ell+1, \dots, \ell-1, \ell \end{cases}$$

Energy scales

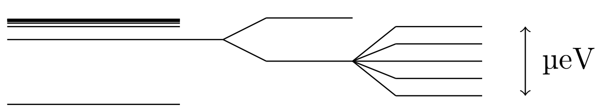
- Energy level structure: $\hat{H}\,|\psi_\alpha\rangle = E_\alpha\,|\psi_\alpha\rangle$



- Relativistic corrections: *fine structure*

Energy scales

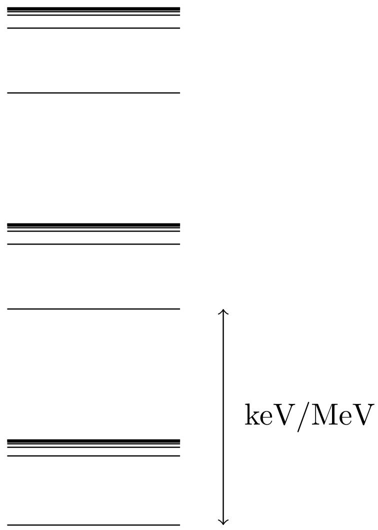
- Energy level structure: $\hat{H}\,|\psi_\alpha\rangle = E_\alpha\,|\psi_\alpha\rangle$



- Relativistic corrections: *fine structure*
- Orientation nucleus in electron cloud: *hyperfine structure*

Energy scales

- Energy level structure: $\hat{H}|\psi_\alpha\rangle = E_\alpha |\psi_\alpha\rangle$
- Nuclear excitations



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Molecular Hamiltonian

- Molecule / solid / defect cluster of:
  - ν nuclei ($\alpha = 1\ldots\nu$) with charge $+Z_\alpha e$ and mass M_α
  - N electrons ($i = 1\ldots N$) with charge $-e$ and mass m_e
- Stationary Schrödinger equation:

$$\hat{H}_{\mathrm{mat}}\Psi(\boldsymbol{r},\boldsymbol{R}) = E\Psi(\boldsymbol{r},\boldsymbol{R})$$

- Nonrelativistic Hamiltonian:

$$\begin{aligned}\hat{H}_{\mathrm{mat}} &= \left[\sum_{\alpha=1}^{\nu}\left(-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \sum_{\beta>\alpha}^{\nu}\frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0\left|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta\right|}\right)\right.\\ &+ \left.\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{\alpha=1}^{\nu}\frac{Z_\alpha e^2}{4\pi\epsilon_0\left|\boldsymbol{R}_\alpha - \boldsymbol{r}_i\right|} + \sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0\left|\boldsymbol{r}_j - \boldsymbol{r}_i\right|}\right)\right]\end{aligned}$$

Born-Oppenheimer approximation

- Ansatz: $\Psi(\boldsymbol{r},\boldsymbol{R}) = \psi(\boldsymbol{r},\boldsymbol{R})\zeta(\boldsymbol{R})$
- Neglect non-adiabatic terms:

$$\hat{H}_{\text{n-ad}} = \sum_{\alpha=1}^{M}\frac{-\hbar^2}{2M_\alpha}\Big(2\nabla_\alpha\psi\left(\boldsymbol{r},R\right)\cdot\nabla_\alpha\zeta(\boldsymbol{R}) + \zeta(\boldsymbol{R})\nabla_\alpha^2\psi(\boldsymbol{r},\boldsymbol{R})\Big),$$

  justified by $M_\alpha \ll m_e$.
- Separation between electronic and nuclear degrees of freedom is obtained
- Born-Oppenheimer approximation = “adiabatic approximation” = “clamped-nuclei approximation”

Born-Oppenheimer approximation

- Electronic eigenvalue equation:

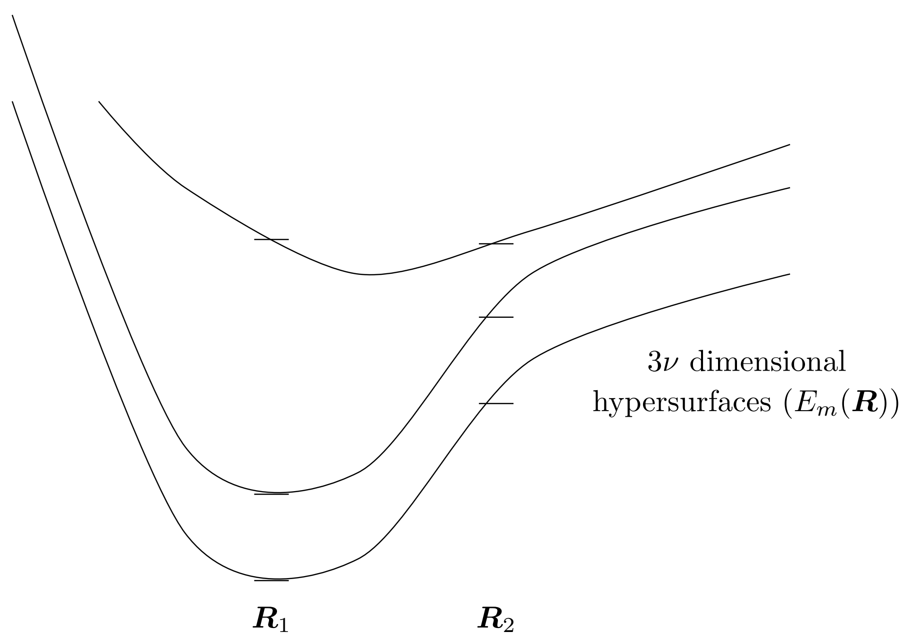
$$\left[\sum_{i=1}^{N}\left(\frac{-\hbar^2}{2m_e}\nabla_i^2-\sum_{\alpha=1}^{\nu}\frac{Z_\alpha e^2}{4\pi\epsilon_0\left|\boldsymbol{R}_\alpha-\boldsymbol{r}_i\right|}+\sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0\left|\boldsymbol{r}_j-\boldsymbol{r}_i\right|}\right)\right.$$
$$\left.+\sum_{\alpha=1}^{\nu}\sum_{\beta>\alpha}^{M}\frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0\left|\boldsymbol{R}_\alpha-\boldsymbol{R}_\beta\right|}\right]\psi_m(\boldsymbol{r},\boldsymbol{R})=E_m\left(R\right)\psi_m(\boldsymbol{r},\boldsymbol{R}),$$

(nuclear coordinates treated as parameters)

- Nuclear/vibrational eigenvalue equation:

$$\left(\sum_{\alpha=1}^{\nu}-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2+E_m(R)\right)\zeta_{m\mu}\left(R\right)=\epsilon_{m\mu}\zeta_{m\mu}\left(R\right).$$

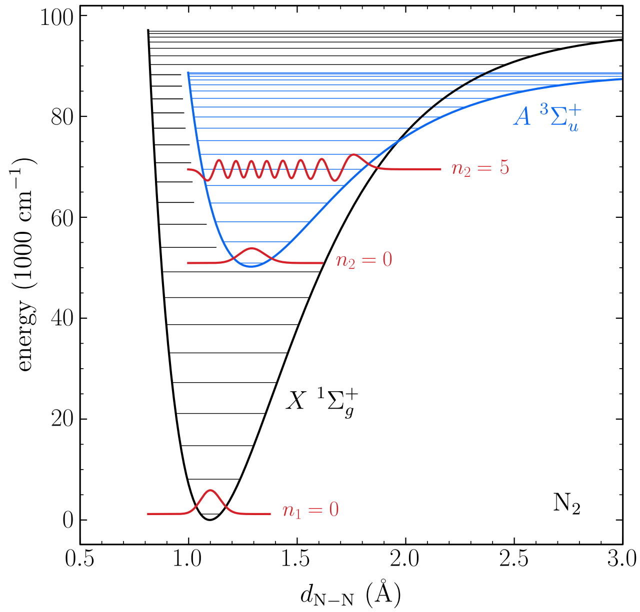
Born-Oppenheimer approximation



Born-Oppenheimer approximation

Example: N_2 molecule

- $\nu = 2$, so $3\nu = 6$: 3 translations; 2 rotations; 1 internal coordinate $d_{\mathrm{N-N}}$



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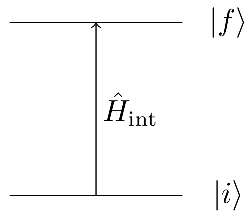
Spectroscopy

Transition probability

- Two level system:



- Fermi's golden rule:

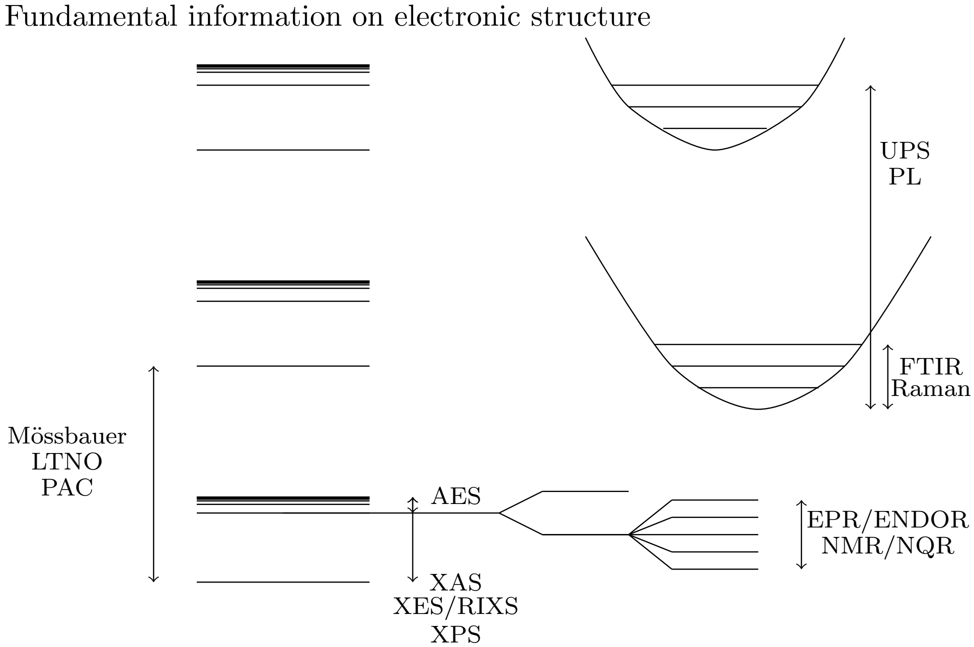
$$W_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | \, \hat{H}_{\text{int}} \, | i \rangle \right|^2 \delta(E_{\text{tot},f} - E_{\text{tot},i})$$

  - Conservation of energy: $E_{\text{tot}} = E_{\text{matter}} + E_{\text{light}}$.
  - $\hat{H}_{\text{int}}$ light-matter interaction

Spectroscopy

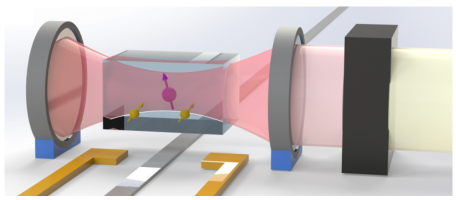
Techniques and energy ranges

- Fundamental information on electronic structure



- Fundamental information on electronic structure
- Light-matter interaction exploited in applications

(a)



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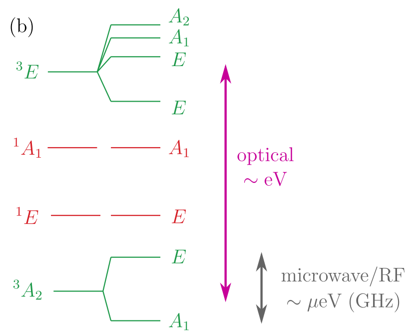

M. Ruf et al., J. Appl. Phys. ***130****, 7 (2021).*