# Van-der-Waals interactions: Theory

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PHASG473 - UCL - ELECTRONIC STRUCTURE METHODS FOR MATERIALS MODELLING

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# Outline of talk

1. Introduction
2. H2 model system
3. Adiabatic connection fluctuation dissipation theorem (ACFDT)
4. Symmetry adapted perturbation theory (SAPT)
5. Generalized PT2

# Recommended literature

- Anthony Stone, *The theory of forces, 2nd ed.*; Oxford University Press, Oxford (2013)
- I. Kaplan, *Intermolecular interactions*; Wiley (2006)
- S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Dispersion-Corrected Mean-Field Electronic Structure Methods*, Chem. Rev.,**116**, 5105 (2016)

Other review articles

- J. Klimeš, A. Michaelides, *Perspective: Advances and challenges in treating van der Waals dispersion forces in density functional theory*, J. Phys. Chem.,**137**, 120901 (2012)
- J. Hoja, A. Reilly, A. Tkatchenko, *First-principles modeling of molecular crystals: structures and stabilities, temperature and pressure*, WIREs Comput. Mol. Sci.,**7** (2017)

# Why are van der Waals interactions important?

- present in all electronic systems; even for non-overlapping densities
- leading term in 3D is always attractive
  $\longrightarrow$ accumulation of “weak” contributions
- London dispersion interaction also known as attractive part of the van der Walls potential

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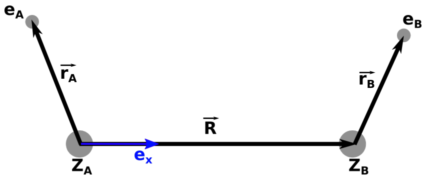
# Definition of the model system



- nuclei fixed, Hilbert space $\mathcal{H}_A = \mathcal{H}_B = \mathcal{L}^2(\mathbb{R}^d)$
- Hamiltonian $\hat{H} = \hat{H}_0^A + \hat{H}_0^B + \hat{H}_I$
- interaction $\hat{H}_I = \frac{1}{R} + \frac{1}{|\mathbf{R} - \mathbf{r}_A + \mathbf{r}_B|} + \frac{1}{|\mathbf{R} - \mathbf{r}_A|} + \frac{1}{|\mathbf{R} + \mathbf{r}_B|}$
- assume R large enough to ignore Fermionic symmetry
- specific form of $\hat{H}_0^{A/B}$ not relevant, only assume rotational symmetry, i.e. $[\hat{H}_0^{A/B}, \hat{U}] = 0$, and $\hat{U}|\Psi(\mathbf{r}_A, \mathbf{r}_B)\rangle = |\Psi(U\mathbf{r}_A, \mathbf{r}_B)\rangle$ rotation matrix $U$ ($\pm 1$ for one dimension)

# Second order perturbation theory

- expand $\hat{H}_I$ in powers of $1/R$:

$$\hat{H}_I = \frac{(\mathbf{r}_A\mathbf{r}_B)R^2 - 3(\mathbf{r}_A\mathbf{R})(\mathbf{r}_B\mathbf{R})}{R^5} = \frac{\mathbf{r}_A\mathbf{r}_B - 3x_Ax_B}{R^3} + \mathcal{O}(R^{-4})$$

- zero order ground state from direct product $|0\rangle = |0_A\rangle|0_B\rangle$
- rotational symmetry $\langle 0_A|\mathbf{r}_A|0_A\rangle = 0$
- zero order energy

$$E_0^0 = \langle 0|\hat{H}_0|0\rangle = E_0^A + E_0^B$$

- first order energy

$$\begin{aligned} E_0^1 =& \langle 0|\hat{H}_I|0\rangle \\ =& \langle 0|\frac{1}{R^3}(\mathbf{r}_A\mathbf{r}_B - 3x_Ax_B|0\rangle + \mathcal{O}(R^{-4}) = 0 + \mathcal{O}(R^{-4}) \end{aligned}$$

# Second order perturbation theory

- second order energy

$$\begin{aligned}
E_0^2 &= -\sum_n{}' \frac{|\langle n|\hat{H}_I|0\rangle|^2}{E_n - E_0} \\
&= -\frac{1}{R^6}\sum_n{}' \frac{|\langle n|\mathbf{r}_A\mathbf{r}_B - 3x_Ax_B|0\rangle|^2}{E_n - E_0} + \mathcal{O}(R^{-8}) \\
&= -\frac{1}{R^6}\sum_{n_A}{}'\sum_{n_B}{}' \frac{|\langle n_An_B|\boldsymbol{\mu}_A\boldsymbol{\mu}_B|0_A0_B\rangle|^2}{E_n^A - E_0^A + E_n^B - E_0^B} + \mathcal{O}(R^{-8}) \\
&= -\frac{6}{R^6}\sum_{n_A}{}'\sum_{n_B}{}' \frac{1}{\omega_{0n}^A + \omega_{0n}^B}\left(|\langle n_A|\mu_A|0_A\rangle|^2|\langle n_B|\mu_B|0_B\rangle|^2\right) + \mathcal{O}(R^{-8})
\end{aligned}$$

- excitation energies $\omega_{0n}^A = E_n^A - E_0^A$, spherical dipole operators $\mu_A$
- MacLachlan integral identity $\frac{1}{A+B} = \frac{2}{\pi}\int \mathrm{d}\omega \frac{AB}{(A^2+\omega^2)(B^2+\omega^2)}$

# Second order perturbation theory

- second order energy

$$E_0^2 = -\frac{1}{R^6}\frac{3}{\pi}\int d\omega \left[\sum_{n_A}{}' \frac{\omega_{0n}^A |\langle n_A|\mu_A|0_A\rangle|^2}{\omega_{0n}^A - (i\omega)^2}\right]\left[\sum_{n_B}{}' \frac{\omega_{0n}^B |\langle n_B|\mu_B|0_B\rangle|^2}{\omega_{0n}^B - (i\omega)^2}\right]$$

$$= -\frac{1}{R^6}\frac{3}{\pi}\int d\omega \alpha^A(i\omega)\alpha^B(i\omega)$$

- dynamical dipole polarizabilities $\alpha^{A/B}$
- dispersion coefficients $C_6^{AB} = \frac{3}{\pi}\int d\omega \alpha^A(i\omega)\alpha^B(i\omega)$
- well known expression for London dispersion energy

$$E_0^2 = -\frac{C_6^{AB}}{R^6}$$

# Absence of $1/R^7$ terms

- inversion operator: $\hat{I}|\Psi(\mathbf{r}_A, \mathbf{r}_B)\rangle = |\Psi(-\mathbf{r}_A, -\mathbf{r}_B)\rangle$
- $\hat{I}$ is symmetry of system: $\left[\hat{I}, \hat{H}\right] = 0$
- $|n\rangle$ are eigenstates of $\hat{I}$, $\hat{I}^2 = 1$, $\hat{I}\mathbf{r}_A\hat{I} = -\mathbf{r}_A$
- split perturbation sum

$$\begin{aligned} E_0^2 &= -\sum_n{}' \frac{|\langle n|\hat{H}_I|0\rangle|^2}{E_n - E_0} \\ &= -\sum_{\substack{n \\ \hat{I}|n\rangle=+|n\rangle}}{}' \frac{|\langle n|\hat{H}_I|0\rangle|^2}{E_n - E_0} - \sum_{\substack{n \\ \hat{I}|n\rangle=-|n\rangle}}{}' \frac{|\langle n|\hat{H}_I|0\rangle|^2}{E_n - E_0} \end{aligned}$$

- no mixed terms of even and uneven power of $R$ possible
  $\longrightarrow$ no $R^{-7}$ term in second order expansion

# Consistency of perturbation expansion

- for consistency, higher oder expansion of $\hat{H}_I$ in first order energy needed
- straight-forward expansion in *Am. J. Phys.* **83**, 150 (2015), App. B
- rewrite first order energy

$$E_0^1 = \langle 0|\hat{H}_I|0\rangle = \langle 0_B|V_A(\mathbf{R}) - V_A(\mathbf{R}+\mathbf{r}_B)|0_B\rangle$$

$$V_A(\mathbf{r}) = \langle 0_A|\frac{1}{r} - \frac{1}{|\mathbf{r}-\mathbf{r}_A|}|0_A\rangle$$

$$= \langle 0_A| - \frac{\mathbf{r}\mathbf{r}_A}{r^3} + \frac{r_A^2}{2r^3} - \frac{3(\mathbf{r}\mathbf{r}_A)^2}{2r^5} + \mathcal{O}(r^{-4})|0_A\rangle$$

- employ identity $\langle 0_A||\mathbf{r}_A|^2|0_A\rangle|\mathbf{r}|^2 = d\langle 0_A||\mathbf{r}\mathbf{r}_A|^2|0_A\rangle$
- characteristic length $a^2 = \frac{\langle 0_A||\mathbf{r}_A|^2|0_A\rangle}{d}$

# Consistency of perturbation expansion

- first order energy

$$E_0^1 = \frac{3(3-d)(5-d)a^2}{4}\frac{1}{R^5} + \mathcal{O}(R^{-7})$$

- for $d = 3$, first oder term vanishes and attractive $R^{-6}$ is the leading order
- for $d = 1, 2$, $E_0^1$ is nonzero and repulsive $R^{-5}$ is the leading order

## Summary: $H_2$ model

- leading order energy: attractive $R^{-6}$ in 3D and repulsive $R^{-5}$ in 1D/2D
- $C_6$ dispersion coefficients can be computed from dynamical polarizabilities of separated atoms

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# Exact expression for correlation energy from response function

$$E_\mathrm{c} = -\frac{1}{2\pi} \int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \int_0^\infty \mathrm{d}\omega \left[\chi_\lambda(\mathbf{r},\mathbf{r}',i\omega) - \chi_0(\mathbf{r},\mathbf{r}',i\omega)\right]$$

- from adiabatic connection fluctuation dissipation theorem[1]
- Coulomb interaction scaled by $\lambda$
- linear response of the electron density with respect to local perturbation

$$\delta\rho(\mathbf{r},\omega) = \int \mathrm{d}\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',i\omega)\, \delta V^\mathrm{ext}(\mathbf{r}',\omega)$$

- relation to dynamic polarizability

$$\alpha_{ij}(i\omega) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\; r_i r_j' \chi(\mathbf{r},\mathbf{r}',i\omega)$$

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[1] A. Zangwill, P. Soven, *Phys. Rev. A* **21**, 1561 (1980)

# In practice not solvable for many-particle systems

$$E_c = -\frac{1}{2\pi}\int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \int_0^\infty \mathrm{d}\omega \left[\chi_\lambda(\mathbf{r},\mathbf{r}',i\omega) - \chi_0(\mathbf{r},\mathbf{r}',i\omega)\right]$$

- analytical expression for non-interaction Kohn-Sham system

$$\chi_0(\mathbf{r},\mathbf{r}',i\omega) = -4\sum_i^{\text{occ}}\sum_a^{\text{virt}} \frac{\omega_{ai}}{\omega_{ai}^2+\omega^2}\varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\varphi_a(\mathbf{r}')\varphi_i(\mathbf{r}')\,,$$

- occupied and virtual KS orbitals $\varphi_i$ and $\varphi_a$
- $\chi_\lambda$ too complicated to compute in practice

  → approximation needed

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# Double perturbation of intra- and interfragment contributions

- start with a HF or KS solution of the unperturbed fragments
- perform a double perturbation in monomer correlation and intermolecular interaction $\hat{H}_I$

$$\hat{H} = \hat{F} + \hat{W} + \hat{H}_I$$

- Fock operator $\hat{F}$, MP perturbation $\hat{W}$
- standard PT not applicable at short distances due to density overlap (product states are no eigenstates of the zero order Hamiltonian)
- use both antisymmetric and symmetric product states

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[2] Claverie, P. "Theory of intermolecular forces. I. On the inadequacy of the usual Rayleigh-Schroödinger perturbation method for the treatment of intermolecular forces." *Int. J. Quantum Chem.* **5**, 273-296 (1971).

# Physical interpretation of different contributions

- different contributions in different order:
  - $E_{\text{es}}^{(1j)}$ 1st order electrostatic
  - $E_{\text{EXR}}^{(1j)}$ 1st order exchange
  - $E_{\text{ind}}^{(2j)}$ 2nd order induction
  - $E_{\text{EXR-ind}}^{(2j)}$ 2nd order exchange induction
  - $E_{\text{ind}}^{(2j)}$ 2nd order dispersion
  - $E_{\text{EXR-disp}}^{(2j)}$ 2nd order exchange dispersion
- gather various orders to physical contribution

$$\Delta E = E_{\text{EXR}} + E_{\text{es}} + E_{\text{ind}} + E_{\text{disp}}$$

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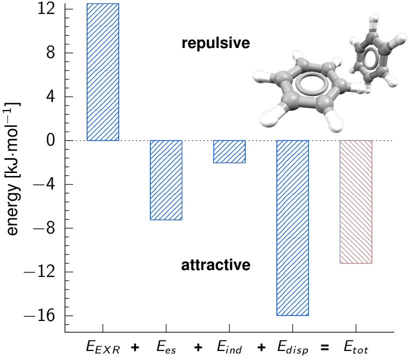
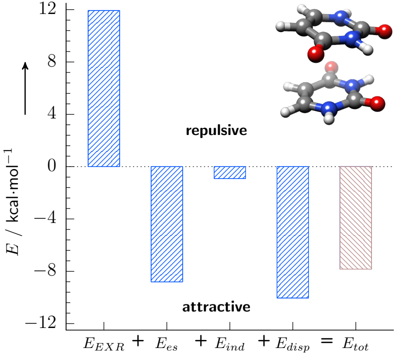
[2] Claverie, P. “Theory of intermolecular forces. I. On the inadequacy of the usual Rayleigh-Schroödinger perturbation method for the treatment of intermolecular forces.” *Int. J. Quantum Chem.* **5**, 273-296 (1971).

# Binding contributions to vdW dimers





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# Rayleigh-Schrödinger PT2

**(1)** Rayleigh-Schrödinger perturbation to second order

$$W^{AB} = W_0^{AB} + W_1^{AB} + W_2^{AB} + \mathcal{O}(3) \tag{1}$$

$$W_0^{AB} = W_0^A + W_0^B \tag{2}$$

$$W_1^{AB} = \langle 00 | V' | 00 \rangle \tag{3}$$

$$\begin{aligned} W_2^{AB} &= -\sum_{mn}{}' \frac{\langle 00 | V' | mn \rangle \langle mn | V' | 00 \rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \\ &= -\sum_{m}{}' \frac{\langle 00 | V' | m0 \rangle \langle m0 | V' | 00 \rangle}{W_0^A - W_m^A} - \sum_{n}{}' \frac{\langle 00 | V' | 0n \rangle \langle 0n | V' | 00 \rangle}{W_0^B - W_n^B} \\ &\quad - \sum_{mn}{}'' \frac{\langle 00 | V' | mn \rangle \langle mn | V' | 00 \rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \end{aligned} \tag{4}$$

# Rayleigh-Schrödinger PT2

**(1)** Rayleigh-Schrödinger perturbation to second order

**(a)** Electrostatic in first order

$$U_{es}^{AB} = \langle 00 | V' | 00 \rangle = \left\langle 00 \;\middle|\; \int \mathrm{d}r\,\mathrm{d}r' \, \frac{\hat{\rho}^A(r)\hat{\rho}^B(r')}{|r - r'|} \;\middle|\; 00 \right\rangle = \int \mathrm{d}r\,\mathrm{d}r' \, \frac{\rho^A(r)\rho^B(r')}{|r - r'|} \quad (5)$$

**(b)** Induction in second order

$$U_{ind}^{A} = -\sum_m{}' \frac{\langle 00 | V' | m0 \rangle \langle m0 | V' | 00 \rangle}{W_0^A - W_m^A}$$

$$U_{ind}^{B} = -\sum_n{}' \frac{\langle 00 | V' | 0n \rangle \langle 0n | V' | 00 \rangle}{W_0^B - W_n^B} \quad (6)$$

# Rayleigh-Schrödinger PT2

**(1)** Rayleigh-Schrödinger perturbation to second oder

**(c)** Dispersion in second order

$$U_{disp}^{AB} = -\sum_{mn}'' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \tag{7}$$

# Multipole expansion

**(2)** Expand $V'$ in Cartesian multipoles

$$\begin{aligned} V' = \;& \mathcal{T} q^A q^B + \mathcal{T}_\alpha \left( q^A \mu_\alpha^B - \mu_\alpha^A q^B \right) \\ & + \mathcal{T}_{\alpha\beta} \left( \frac{1}{3} q^A \Theta_{\alpha\beta}^B - \mu_\alpha^A \mu_\beta^B + \frac{1}{3} \Theta_{\alpha\beta}^A q^B \right) + \mathcal{O}(n^3) \end{aligned} \tag{8}$$

$$\mathcal{T}^n_{\alpha\beta\ldots\nu} = \nabla_\alpha \nabla_\beta \ldots \nabla_\nu \left( \frac{1}{R} \right) \tag{9}$$

more compact in spherical harmonics

$$V' = \mathcal{Q}^A_{l_1 m_1} \mathcal{T}_{l_1 m_1, l_2 m_2} \mathcal{Q}^B_{l_2 m_2} \tag{10}$$

summation over identical indices always implied

# Multipole expansion in PT2

**(1+2)** For simplicity start with dipole-dipole term

$$
\begin{aligned}
U^{AB}_{disp} &= -\sum_{m_A \neq 0}\sum_{n_B \neq 0} \frac{\langle 0_A 0_B | \mu^A_\alpha \mathcal{T}_{\alpha\beta} \mu^B_\beta | m_A n_B \rangle \langle m_A n_B | \mu^A_\gamma \mathcal{T}_{\gamma\delta} \mu^B_\delta | 0_A 0_B \rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= -\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta} \sum_{m_A \neq 0}\sum_{n_B \neq 0} \frac{\langle 0_A | \mu^A_\alpha | m_A \rangle \langle m_A | \mu^A_\gamma | 0_A \rangle \langle 0_B | \mu^B_\beta | n_B \rangle \langle n_B | \mu^B_\delta | 0_B \rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= -\frac{2}{\pi}\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta} \int \mathrm{d}\omega \left[ \sum_m{}' \frac{\omega^A_m \langle 0_A | \mu^A_\alpha | m_A \rangle \langle m_A | \mu^A_\gamma | 0_A \rangle}{{\omega^A_m}^2 + \omega^2} \right. \\
&\qquad \left. \times \sum_n{}' \frac{\omega^B_n \langle 0_B | \mu^B_\beta | n_B \rangle \langle n_B | \mu^B_\delta | 0_B \rangle}{{\omega^B_n}^2 + \omega^2} \right] \qquad (11)
\end{aligned}
$$

Use McLachlan integral identity to factorize energy denominator

$$
\frac{1}{A+B} = \frac{2}{\pi}\int \mathrm{d}\omega \, \frac{AB}{(A^2+\omega^2)(B^2+\omega^2)} \qquad (12)
$$

# Multipole expansion in PT2

**(1+2)** Identify dynamic polarizability

$$U_{disp}^{AB} = -\frac{2}{\pi}\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta}\int \mathrm{d}\omega\, \alpha^{A}_{\alpha\gamma}(i\omega)\,\alpha^{B}_{\beta\delta}(i\omega) \tag{13}$$

Spherical averaging (exact for atoms)

$$U_{disp}^{AB} = -\frac{3}{\pi}\int \mathrm{d}\omega\, \overline{\alpha}^{A}(i\omega)\,\overline{\alpha}^{B}(i\omega) \times \frac{1}{R^6} = -\frac{C_6^{AB}}{R^6} \tag{14}$$

Analogue for higher order terms, short-range damping

$$U_{disp}^{AB} = = \sum_{n=6,8,10,\ldots} \frac{C_n^{AB}}{R^n} f_{damp}^{(n)} \tag{15}$$

More general via charge density susceptibility

$$U_{disp}^{AB} = -\frac{1}{2\pi}\int \mathrm{d}\omega \int \mathrm{d}r_a\,\mathrm{d}r'_a\,\mathrm{d}r_b\,\mathrm{d}r'_b\, \frac{\chi(r_a, r'_a, i\omega)\chi(r_b, r'_b, i\omega)}{|r_a - r_b||r'_a - r'_b|} \tag{16}$$