Ab initio force fields for non-covalent interactions

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Outline:

- Preamble: Born-Oppenheimer approximation
- What are non-covalent interactions?
  Quantum mechanical derivation
- How to compute intermolecular force fields *ab initio*?
- How to test intermolecular force fields?
  Van der Waals molecules, spectra
- Illustration: *ab initio* force field for water, applications

Concepts:

- Molecular force fields (MM calculations)
- Interatomic / intermolecular forces (potential energy surfaces)
- Forces on atoms in solids
- Equilibrium structures, force constants
- Chemical reaction paths (from QM calculations)

Exist only in Born-Oppenheimer approximation

Born-Oppenheimer (adiabatic) approximation

Step 1:

Solve electronic Schrödinger equation

$$H_{\mathrm{e}}\,\phi(\mathbf{r};\mathbf{R}) = E_{\mathrm{e}}(\mathbf{R})\,\phi(\mathbf{r};\mathbf{R})$$

for nuclei fixed at positions $\mathbf{R}$.

Involves neglect of nuclear kinetic energy T_{n}.

Step 2:

Solve nuclear Schrödinger equation

$$[T_{\mathrm{n}} + E_{\mathrm{e}}(\mathbf{R})]\,\chi(\mathbf{R}) = E\chi(\mathbf{R})$$

with potential energy surface $E_{\mathrm{e}}(\mathbf{R})$

$\Rightarrow$ vibrations, rotations, (phonons, librations),
chemical reaction dynamics, molecular collisions.

Alternative for step 2

Molecular dynamics (MD):

solve nuclear motions classically on potential surface $E_{\mathrm{e}}(\mathbf{R})$.

What are non-covalent interactions?

QM derivation