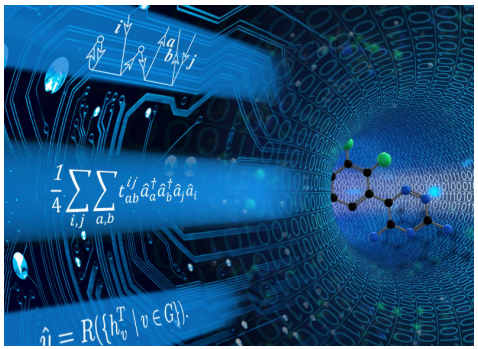
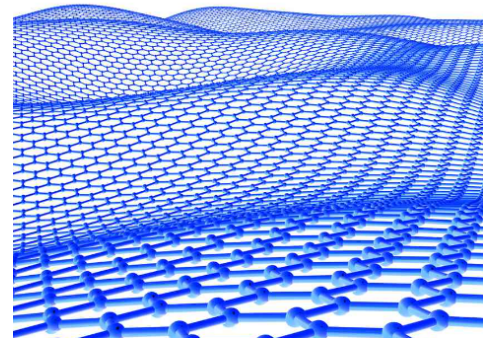
# Mathematical foundations of modern quantum simulations

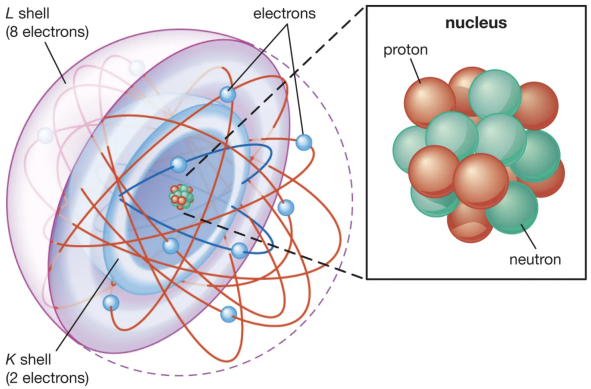




Fabian M. Faulstich

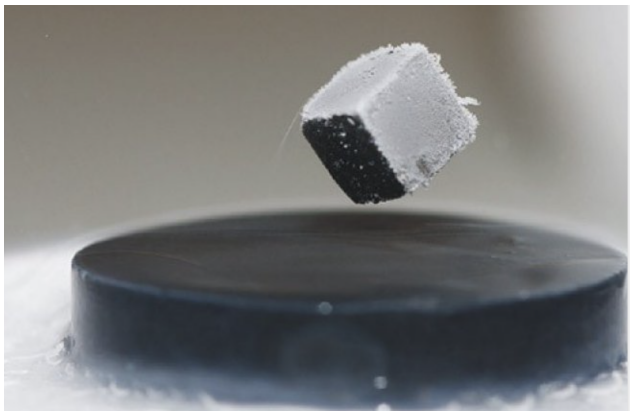
Department of Mathematics, Rensselaer Polytechnic Institute, Troy, NY

# What are quantum simulations?

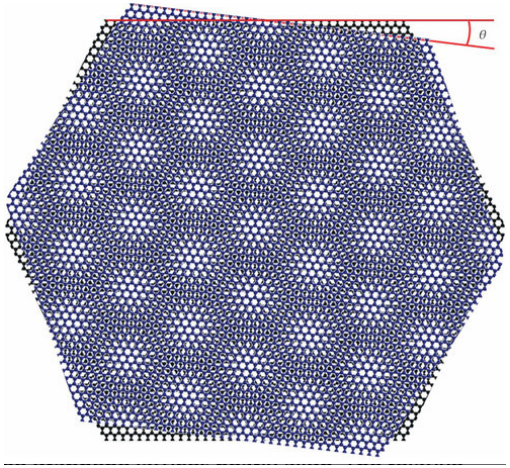



Stability of matter

Color of gold

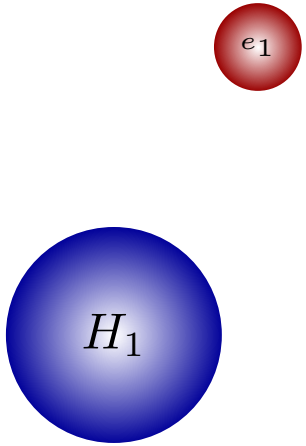


Superconductivity




Solid state physics

# Towards a mathematical formulation



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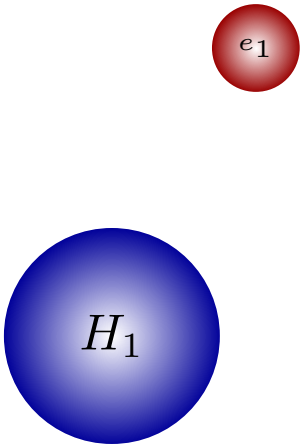
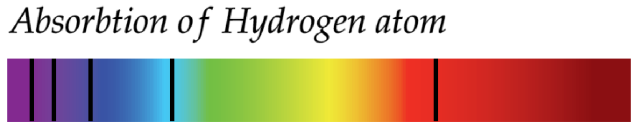
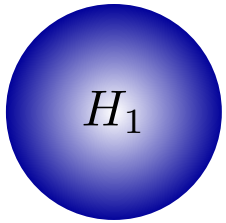



# Towards a mathematical formulation

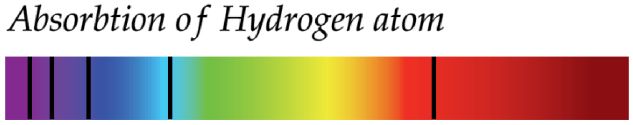



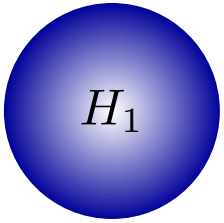




Two energetic contributions:

1. Kinetic energy: $h_{\text{kin}} = -\frac{1}{2}\Delta$
2. Coulomb energy: $V_{\text{coul}} = -\frac{1}{|r - R|}$

# Towards a mathematical formulation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1. Kinetic energy: $h_{\text{kin}} = -\frac{1}{2}\Delta$
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Birth of quantum chemistry[a]:

$$\Delta\psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

[a] Schrödinger, Annalen der physik (1926)

# Schrödinger equation

The goal is to solve

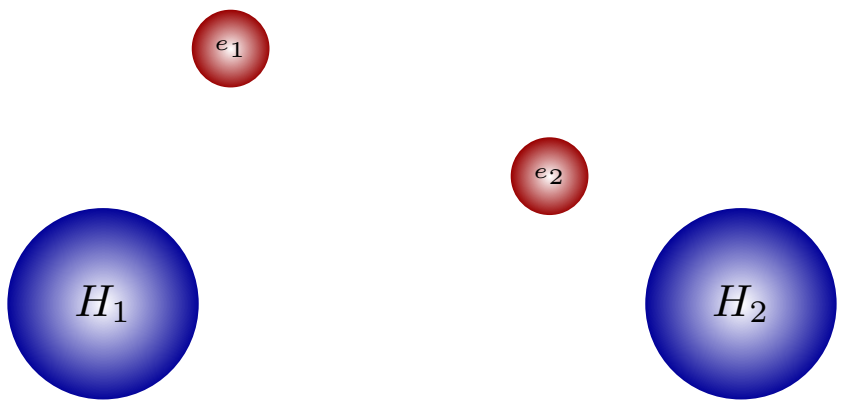
$$H\Psi = E\Psi,$$

where

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_{r_i} - \sum_{i=1}^{N}\sum_{j=1}^{N_{\text{nuc}}}\frac{Z_j}{|r_i - R_j|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|r_i - r_j|}$$

and $\Psi$ is a function defined on $\mathbb{R}^{3N}$ for $N$ electrons.

$r_i$ position of the i$th$ electron
$R_j$, $Z_j$ position (fixed) and charge of the j$th$ nucleus



# What is the problem?

Discretization scales *exponentially* in the number of electrons $N$

[1] The estimated number of particles in the universe is $\sim 10^{80}$

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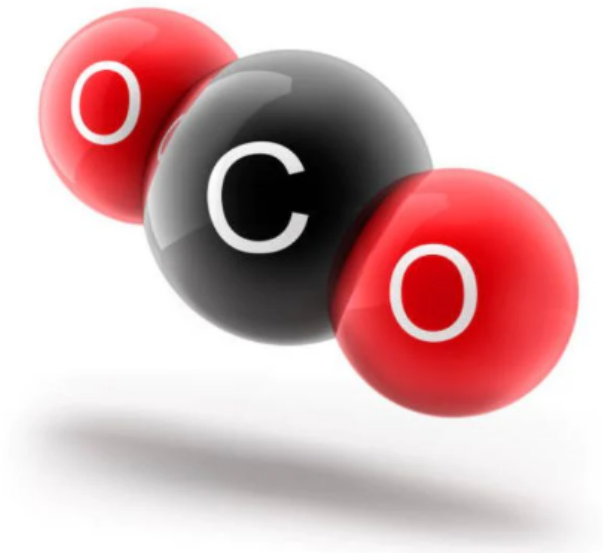
Example: carbon dioxide ($CO_2$)

Oxygen has 8 electrons

Carbon has 6 electrons

In total: $N = 2 * 8 + 6 = 22$

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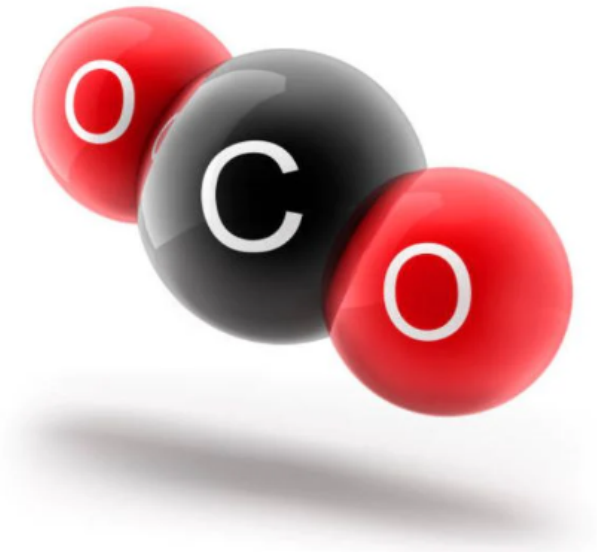


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Naïve grid with 10 points per axis yields $10^{3 \cdot 22} = 10^{66}$ grid points[1]

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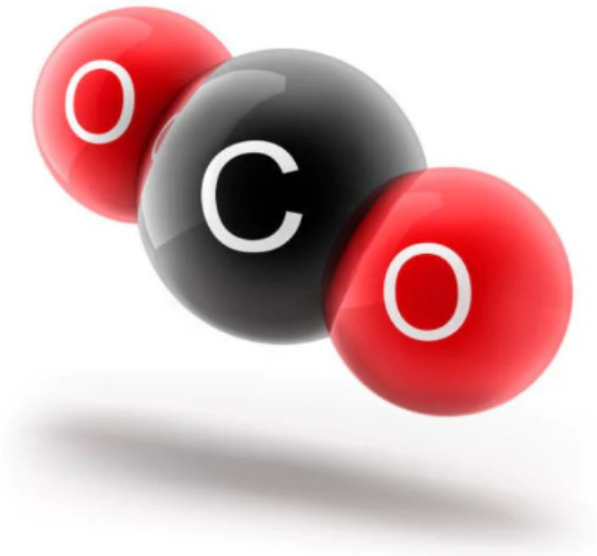


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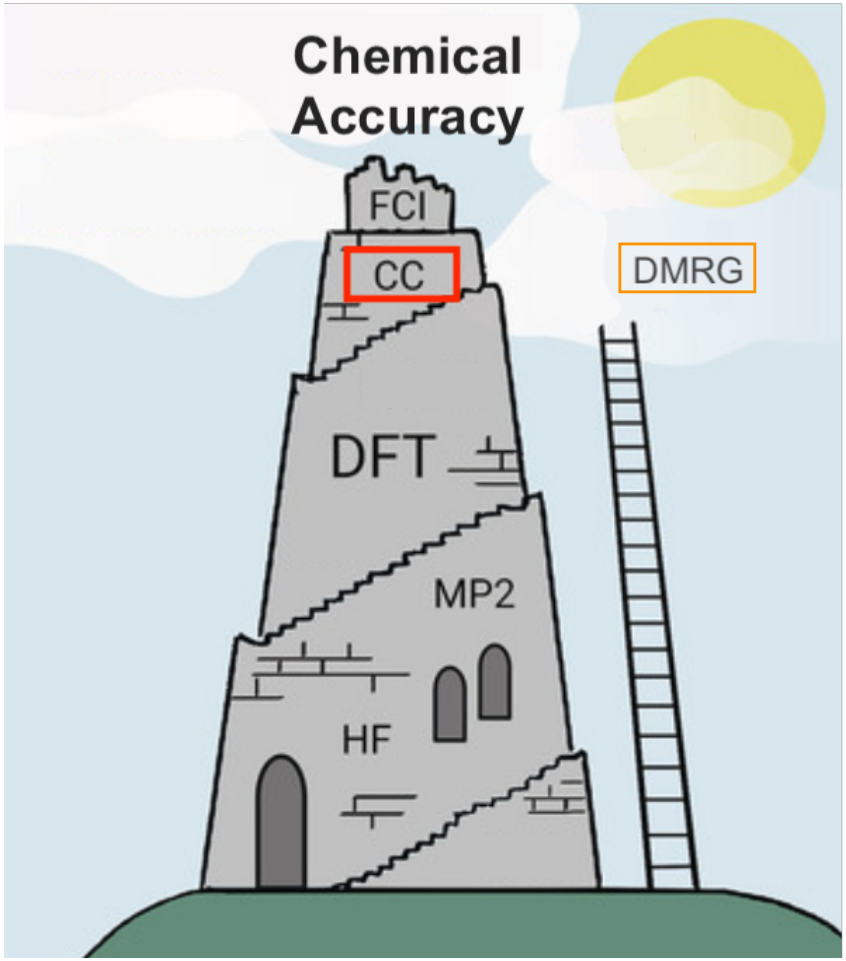
In total: $N = 2 * 8 + 6 = 22$

Naïve grid with 10 points per axis yields $10^{3 \cdot 22} = 10^{66}$ grid points[1]

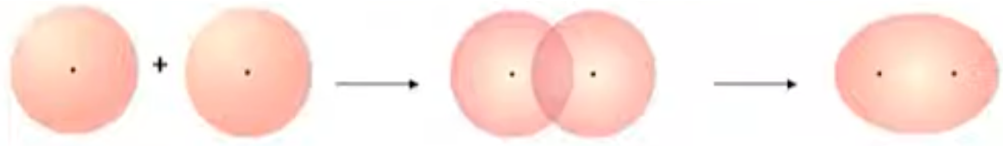
$\Rightarrow$ Approximation is key!

[1] The estimated number of particles in the universe is $\sim 10^{80}$

# Quantum chemical methods



# Strongly correlated quantum chemistry



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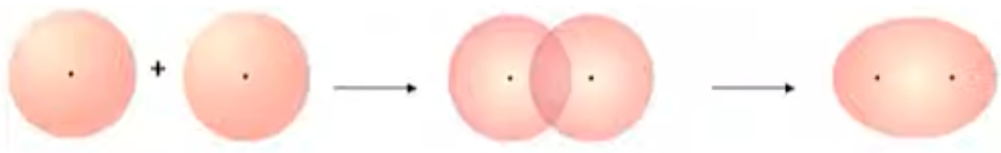
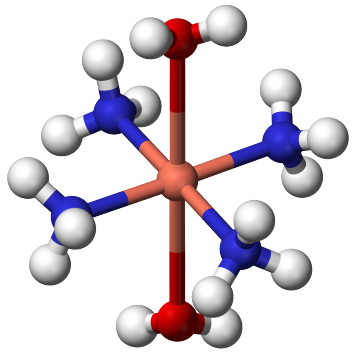
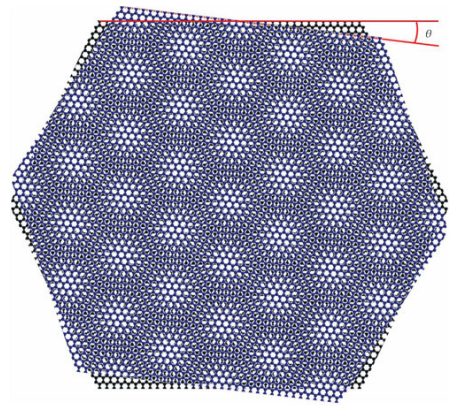


This happens at various scales


Small molecules



Transition metal complexes



Twisted bilayer graphene

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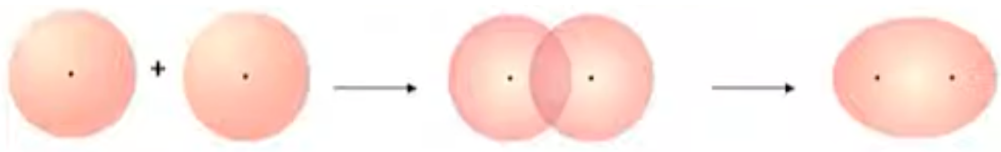

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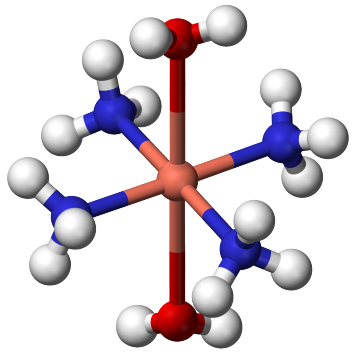

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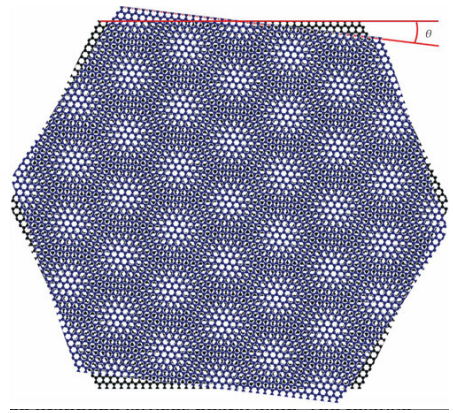

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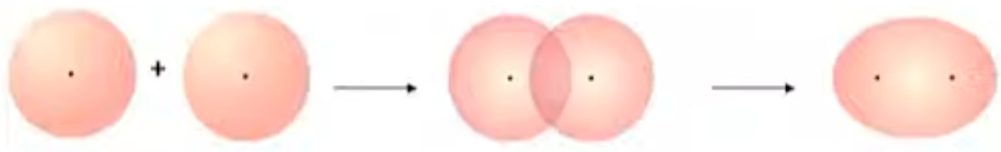
Strongly correlated systems are *very* difficult to compute

# Strongly correlated quantum chemistry



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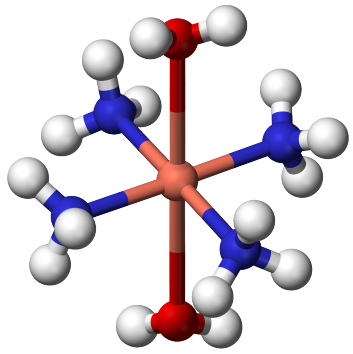

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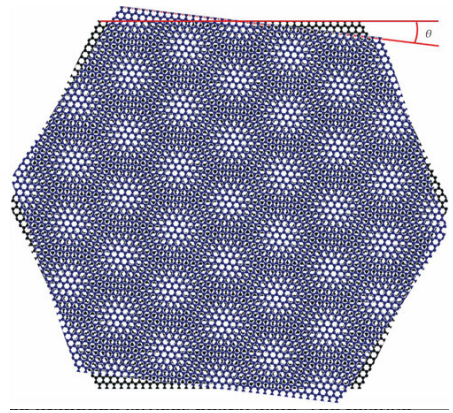


Twisted bilayer graphene

Strongly correlated systems are *very* difficult to compute
Important failure modes for existing methods

$\Rightarrow$ The research frontier of computational chemistry lies in strongly correlated systems

# Roadmap

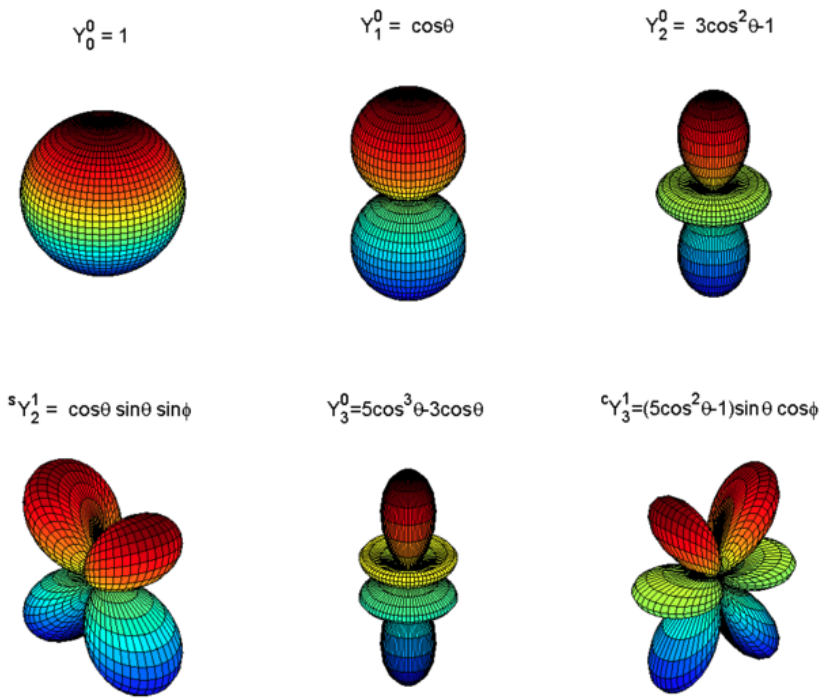
1. Quantum mechanics of the hydrogen atom
2. The hydrogen molecule and the Hartree-Fock method
3. Second quantization I
4. Second quantization II
5. Second quantization III
6. The linear combination of atomic orbitals ansatz
7. Gaussian-type atomic orbitals and high-dimensional integration
8. Size consistency and the coupled cluster ansatz
9. Truncating the coupled cluster ansatz and its working equations
10. Finding one root to the coupled cluster equations
11. Finding all roots to the coupled cluster equations

# Quantum mechanics of the hydrogen atom

Analytic solution to the eigenvalue problem

$$\left(\frac{1}{2}\Delta_r + \frac{1}{|r-R|}\right)\Psi(r) = -E\Psi(r)$$

3D partial differential equation!



# The hydrogen molecule and the Hartree-Fock method

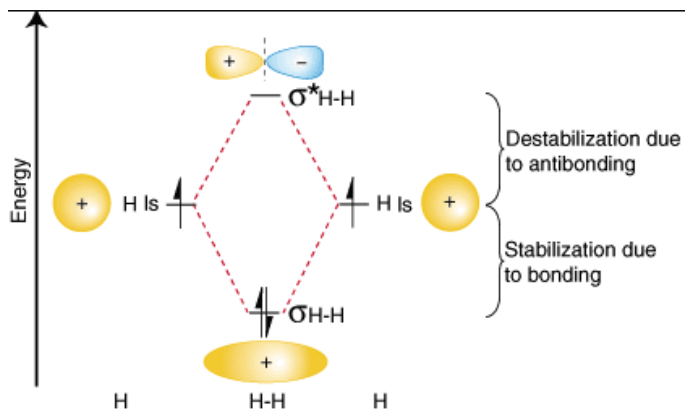
The Hamiltonian reads

$$H = -\frac{1}{2}\Delta_{r_1} - \frac{1}{|r_1 - R_1|} - \frac{1}{2}\Delta_{r_2} - \frac{1}{|r_2 - R_2|} - \frac{1}{|r_2 - R_1|} - \frac{1}{|r_1 - R_2|} + \frac{1}{|r_1 - r_2|}$$

we want to solve

$$H\Psi(r_1, r_2) = E\Psi(r_1, r_2)$$

$\Rightarrow$ Not possible!



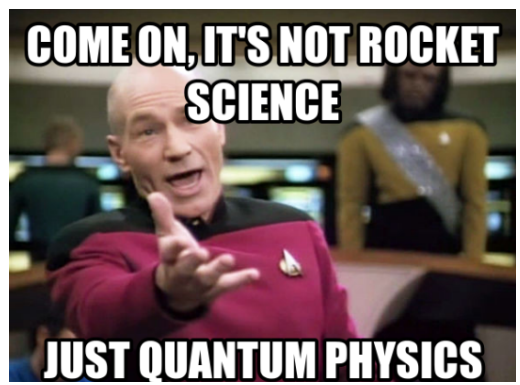
# Second quantization I:

## Fock space, creation and annihiliation operators, CAR algebra

High-dimensional PDE's are hard!

- Can we think of matrices instead?
- Can we manipulate these matrices fast?

# Second Quantization



# Second quantization II:

## Excitation operators, CCR algebra, nilpotent Lie algebra

The second quantization shows its teeth

# Second quantization III:

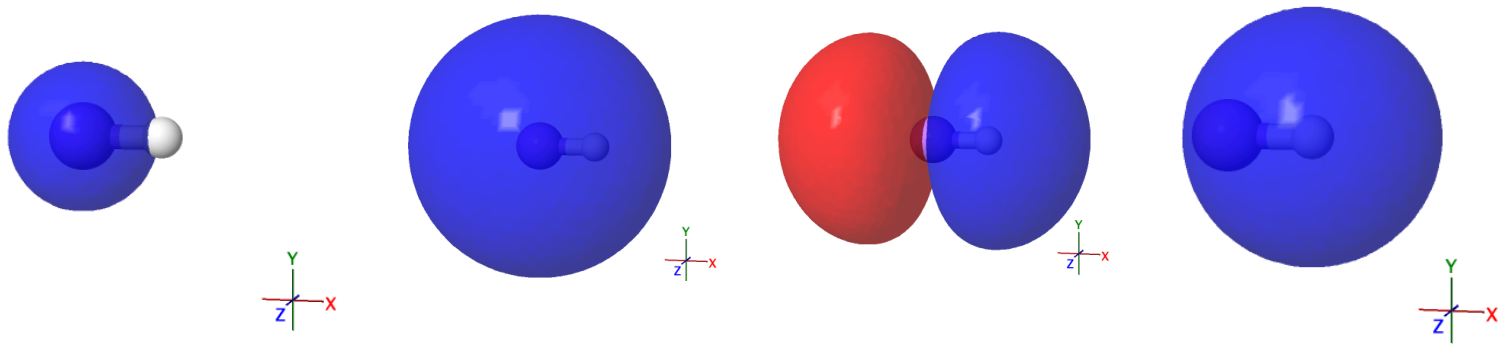
## Slater-Condon rules, Wick's theorem, Hartree-Fock revisited

Let's bring out the big guns...

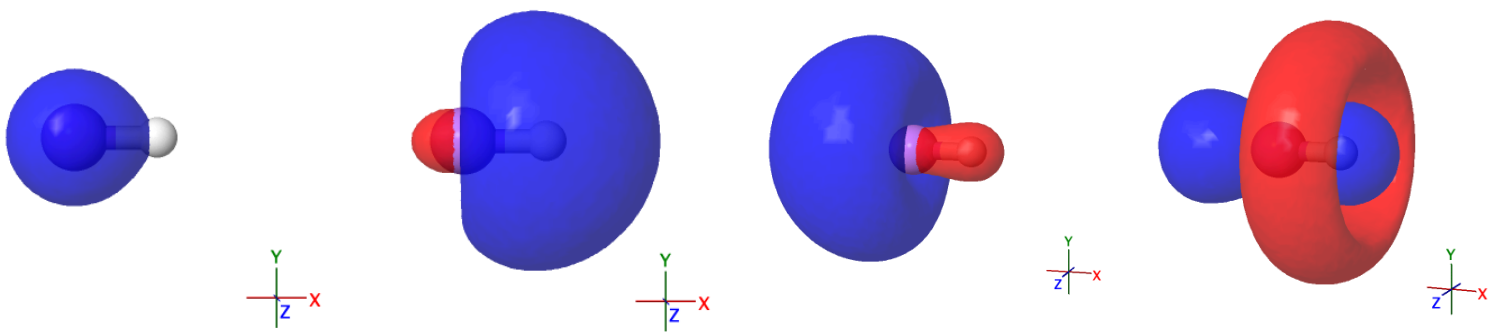
(Wick'ed guys)

# The linear combination of atomic orbitals ansatz

Atomic orbitals



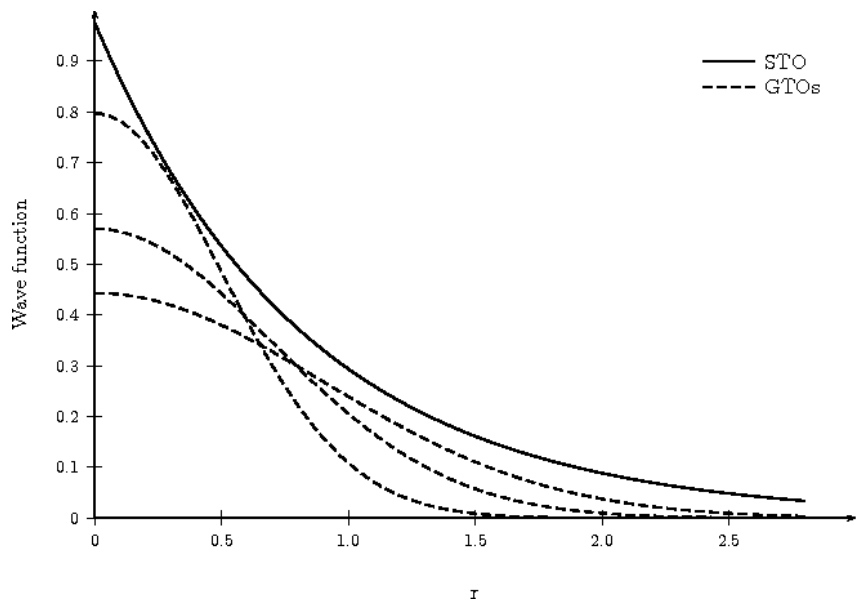

Molecular orbitals



# Gaussian-type atomic orbitals and high-dimensional integration

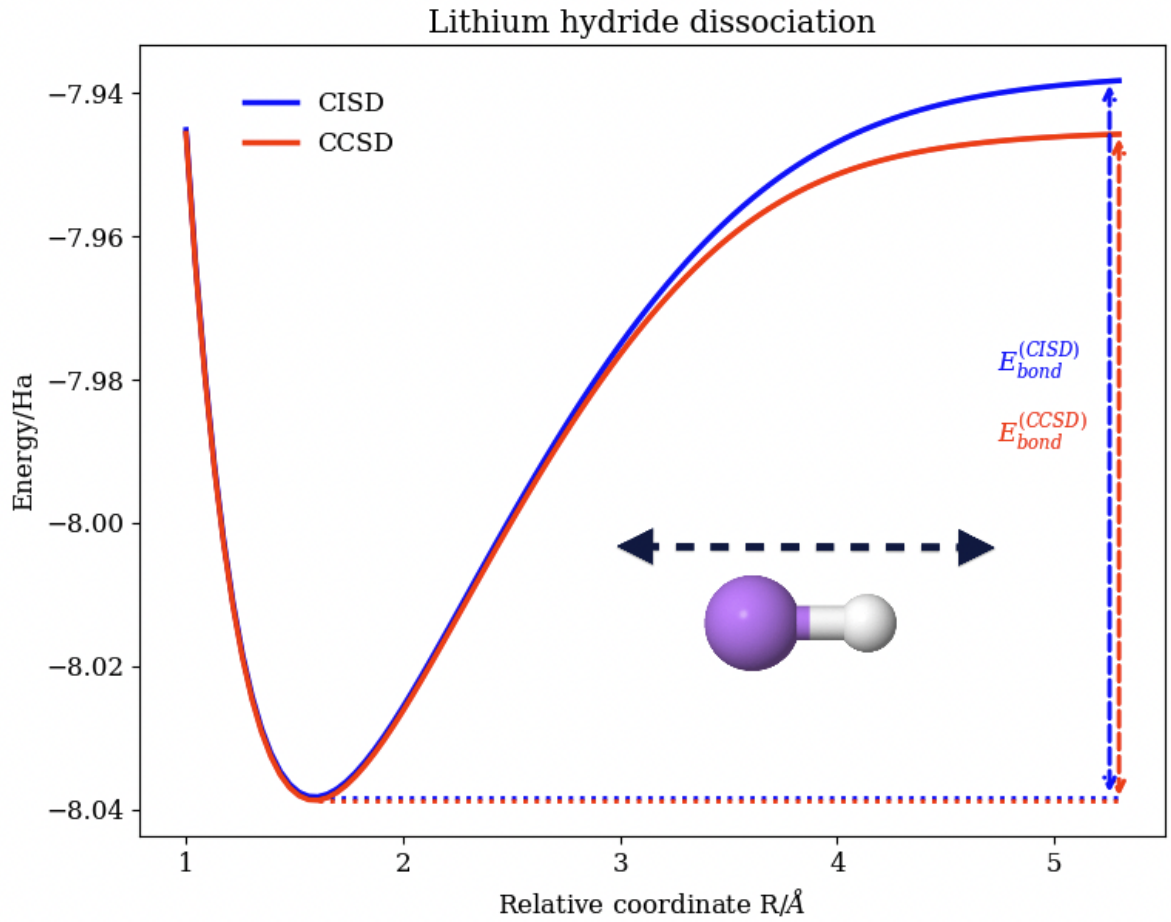
We will face the following integral evaluation:

$$v_{p,q,r,s} = \int_{X\times X} \frac{\xi_p^*(x_1)\xi_q(x_1)\xi_r^*(x_2)\xi_s(x_2)}{|r_1 - r_2|} d\lambda(x) d\lambda(x),$$



# Size consistency and the coupled cluster ansatz

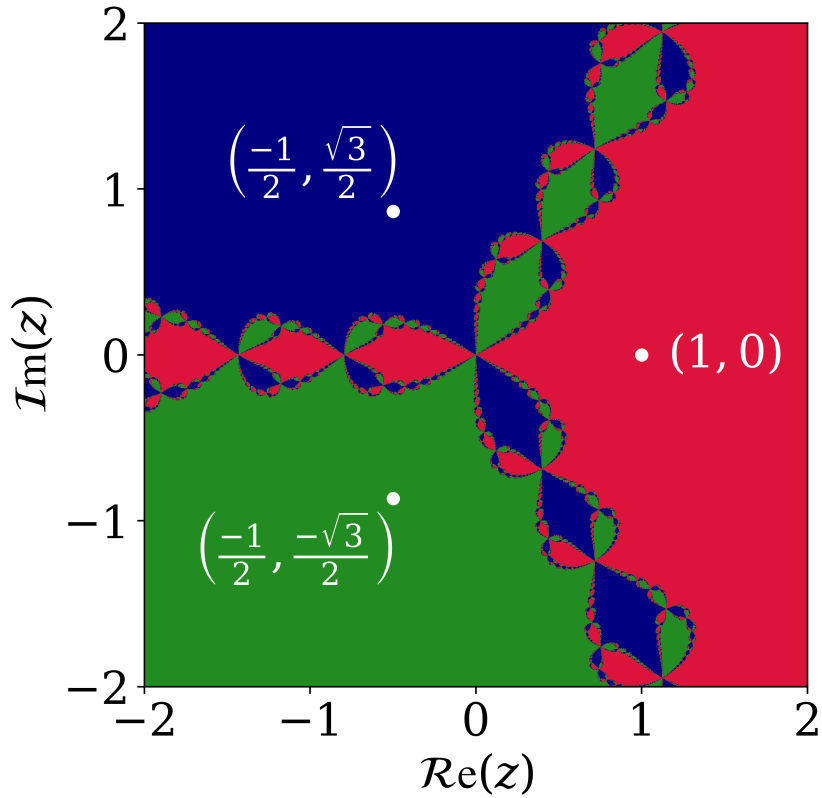
What do we really care about?



# Truncating the coupled cluster ansatz and its working equations

$$
\begin{aligned}
E(t) &= \langle \Psi_0, H\Psi_0 \rangle + \sum_{IA} f_{IA} t_I^A + \frac{1}{4} \sum_{IJAB} \langle IJ \| AB \rangle t_{IJ}^{AB} + \frac{1}{2} \sum_{IJAB} \langle IJ \| AB \rangle t_I^A t_J^B, \\
f(t)_I^A &= f_{IA} + \sum_C f_{AC} t_I^C - \sum_K f_{KI} t_K^A + \sum_{KC} \langle KA \| CI \rangle t_C^K + \sum_{KC} f_{KC} t_{IK}^{AC} \\
&+ \frac{1}{2} \sum_{KCD} \langle KA \| CD \rangle t_{KI}^{CD} - \frac{1}{2} \sum_{KLC} \langle KL \| CI \rangle t_{KL}^{CA} - \sum_{KC} f_{KC} t_I^C t_K^A - \sum_{KLC} \langle KL \| CI \rangle t_K^C t_L^A \\
&+ \sum_{KCD} \langle KA \| CD \rangle t_K^C t_I^D - \sum_{KLCD} \langle KL \| CD \rangle t_K^C t_I^D t_L^A + \sum_{KLCD} \langle KL \| CD \rangle t_C^K t_{LI}^{DA} \\
&- \frac{1}{2} \sum_{KLCD} \langle KL \| CD \rangle t_{KI}^{CD} t_L^A - \frac{1}{2} \sum_{KLCD} \langle KL \| CD \rangle t_{KL}^{CA} t_I^D \\
f(t)_{IJ}^{AB} &= \langle IJ \| AB \rangle + \sum_C \left( f_{BC} t_{IJ}^{AC} - f_{AC} t_{IJ}^{BC} \right) - \sum_K \left( f_{KJ} t_{IK}^{AB} - f_{KI} t_{JK}^{AB} \right) \\
&+ \frac{1}{2} \sum_{KL} \langle KL \| IJ \rangle t_{KL}^{AB} + \frac{1}{2} \sum_{CD} \langle AB \| CD \rangle t_{IJ}^{CD} + P(IJ)P(AB) \sum_{KC} \langle KB \| CJ \rangle t_{IK}^{AC} \\
&+ P(IJ) \sum_C \langle AB \| CJ \rangle t_I^C - P(AB) \sum_K \langle KB \| IJ \rangle t_A^K \\
&+ \frac{1}{2} P(IJ)P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_{IK}^{AC} t_{LJ}^{DB} + \frac{1}{4} \sum_{KLCD} \langle KL \| CD \rangle t_{IJ}^{CD} t_{KL}^{AB} \\
&+ \frac{1}{2} P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_{IJ}^{AC} t_{KL}^{BD} - \frac{1}{2} P(IJ) \sum_{KLCD} \langle KL \| CD \rangle t_{IK}^{AB} t_{JL}^{CD} \\
&+ \frac{1}{2} P(AB) \sum_{KL} \langle KL \| IJ \rangle t_K^A t_L^B + \frac{1}{2} P(IJ) \sum_{CD} \langle AB \| CD \rangle t_I^C t_J^D \\
&- P(IJ)P(AB) \sum_{KC} \langle KB \| IC \rangle t_K^A t_J^C + P(AB) \sum_{KC} f_{KC} t_K^A t_{IJ}^{BC} \\
&+ P(IJ) \sum_{KC} f_{KC} t_I^C t_{JK}^{AB} - P(IJ) \sum_{KLC} \langle KL \| CI \rangle t_K^C t_{LJ}^{AB} \\
&+ P(AB) \sum_{KCD} \langle KA \| CD \rangle t_K^C t_{IJ}^{DB} + P(IJ)P(AB) \sum_{KCD} \langle AK \| DC \rangle t_I^D t_{JK}^{BC} \\
&+ P(IJ)P(AB) \sum_{KLC} \langle KL \| IC \rangle t_L^A t_{JK}^{BC} + \frac{1}{2} P(IJ) \sum_{KLC} \langle KL \| CJ \rangle t_I^C t_{KL}^{AB} \\
&- \frac{1}{2} P(AB) \sum_{KCD} \langle KB \| CD \rangle t_K^A t_{IJ}^{CD} + \frac{1}{2} P(IJ)P(AB) \sum_{KLC} \langle KB \| CD \rangle t_I^C t_K^A t_J^D \\
&+ \frac{1}{2} P(IJ)P(AB) \sum_{KLC} \langle KL \| CJ \rangle t_I^C t_K^A t_L^B - P(IJ) \sum_{KLCD} \langle KL \| CD \rangle t_K^C t_I^D t_{LJ}^{AB} \\
&- P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_K^C t_L^A t_{IJ}^{DB} - \frac{1}{4} P(IJ) \sum_{KLCD} \langle KL \| CD \rangle t_I^C t_J^D t_{KL}^{AB} \\
&+ \frac{1}{4} P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_K^A t_L^B t_{IJ}^{CD} + P(IJ)P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_I^C t_L^B t_{KJ}^{AD} \\
&+ \frac{1}{4} P(IJ)P(AB) \sum_{KLCD} \langle KL \| CD \rangle t_I^C t_K^A t_J^D t_L^B
\end{aligned}
$$

# Finding one root to the coupled cluster equations



# Finding all roots to the coupled cluster equations

Seeking:

$$f(\mathrm{t}) = \begin{bmatrix} f_1(\mathrm{t}) \\ \vdots \\ f_m(\mathrm{t}) \end{bmatrix} = \begin{bmatrix} f_1(t_1, ..., t_m) \\ \vdots \\ f_m(t_1, ..., t_m) \end{bmatrix} = 0.$$

Find a start system $g$, and then continuously deform $g$ into $f$

Davidenko differential equation:

$$\frac{\partial}{\partial \mathrm{t}} H(\mathrm{t}, \lambda) \left( \frac{\mathrm{d}}{\mathrm{d}\lambda} \mathrm{t}(\lambda) \right) + \frac{\partial}{\partial \lambda} H(\mathrm{t}, \lambda) = 0, \quad \mathrm{t}(1) = \mathrm{s}_0,$$

# Finding all roots to the coupled cluster equations

Seeking:

$$f(\mathrm{t}) = \begin{bmatrix} f_1(\mathrm{t}) \\ \vdots \\ f_m(\mathrm{t}) \end{bmatrix} = \begin{bmatrix} f_1(t_1, ..., t_m) \\ \vdots \\ f_m(t_1, ..., t_m) \end{bmatrix} = 0.$$