The very basic: QF methods and many body perturbation theory

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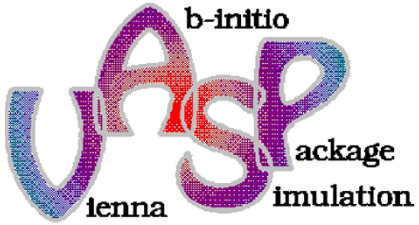
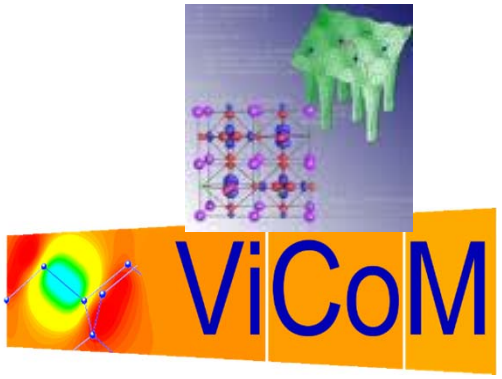
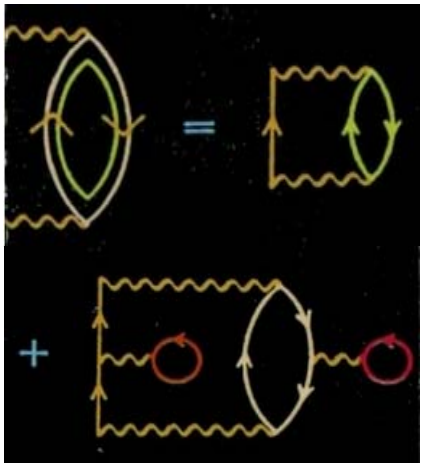




Outline

- Introduction
  - DFT and why not only DFT
- Many-body Perturbation Theory
  - Particle/hole picture, Gell-Man – Low theorem Wick theorem, and Linked cluster theorem
  - Derivation of Goldstone diagrams
  - Derivation of Feynman diagrams



- Reading
  - Szabo and Ostlun, *Modern Quantum Chemistry* (McGraw-Hill, 1989)
  - Shavitt and Bartlett, *Many-body methods in chemistry and physics* (Cambridge University Press, 2009)
  - Lancaster, Blundell, Stephen, *Quantum field theory for the gifted amateur* (Oxford University Press, 2014)

Schrödinger's Inheritance

„Ab initio“↔ parameter free ↔

Many electron
Schrödinger equation is an
exponentially complex problem

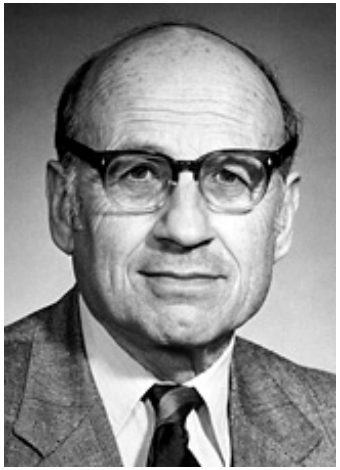
linear partial differential equation with non polynomial (NP) complexity (NP hard)

$$H^{\text{el}}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = -\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} - \sum_{i=1}^{N}V^{\text{ne}}(\mathbf{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

$$H^{\text{el}}\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n) = E\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)$$

Schrödinger's Curse: $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots)$

- One electron: 3D-grid 10x10x10 16 Kbyte
- Three electrons: 9D-grid 10^9 16 Gbye
- Five electrons: 15D-grid 10^{30} 16.000 Terrabyte

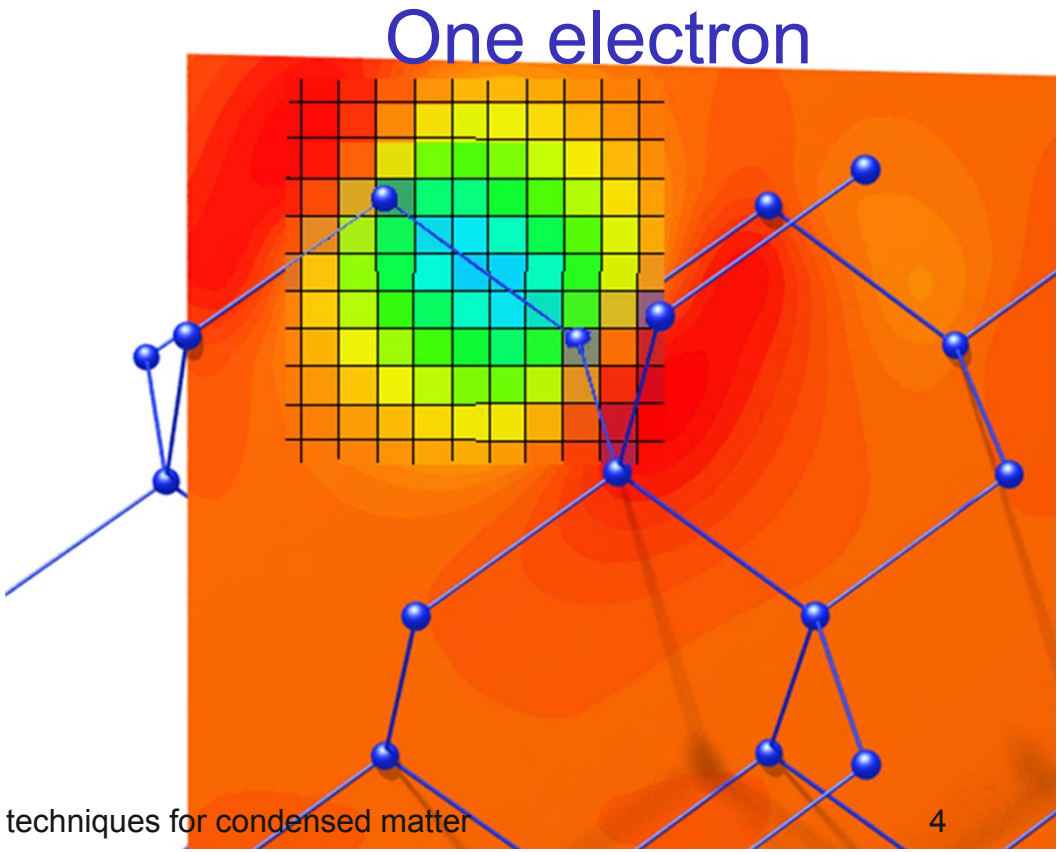


W. Kohn

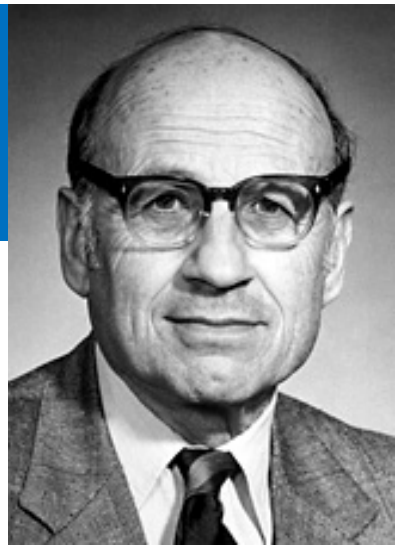
five electrons

five 3D sets

- 1923 Vienna
- 1940 Canada (Kindert.)
- 1950 Carnegien Mellon
- 1984 Santa Barabara
- 1998 Nobel Preis



Kohn Sham Density functional and Hartree-Fock one electron theory



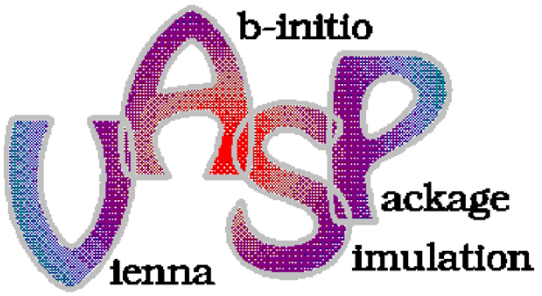
Solve a one-particle Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{r})\right)\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r}) \quad \mathbf{H}\phi_n = \varepsilon_n\phi_n$$

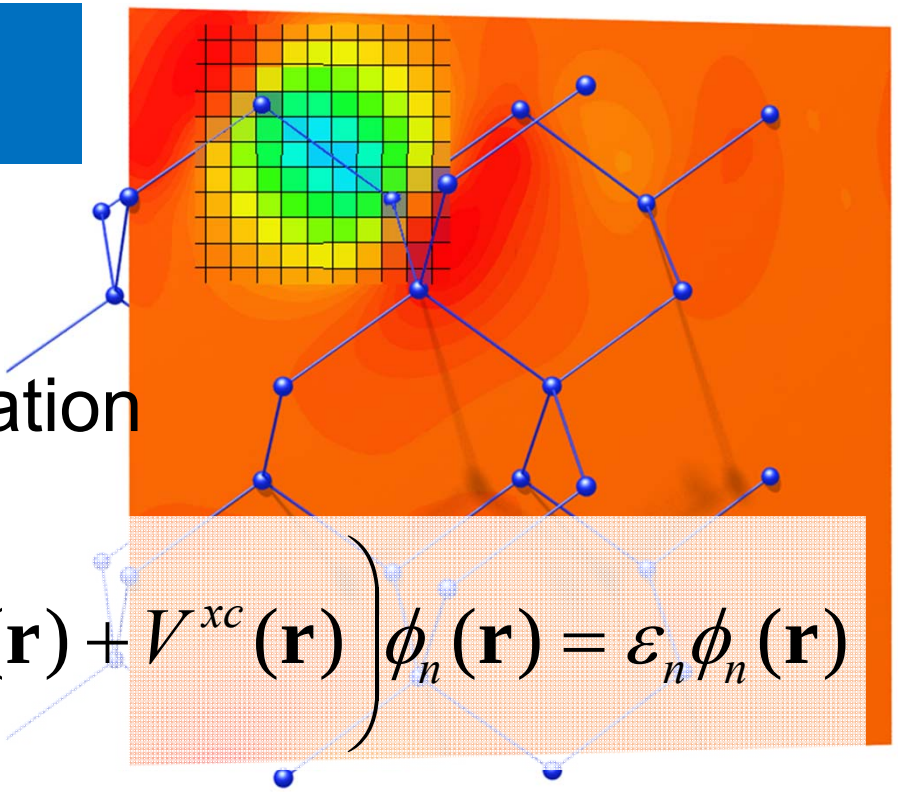
N orbitals corresponding to N electrons need to be calculated

$$\{\phi_n(\mathbf{r}), n = 1,\ldots,N\}$$

Non-linear partial differential equation
complexity N^3



So what does DFT do



Kohn-Sham DFT
uses a one electron equation

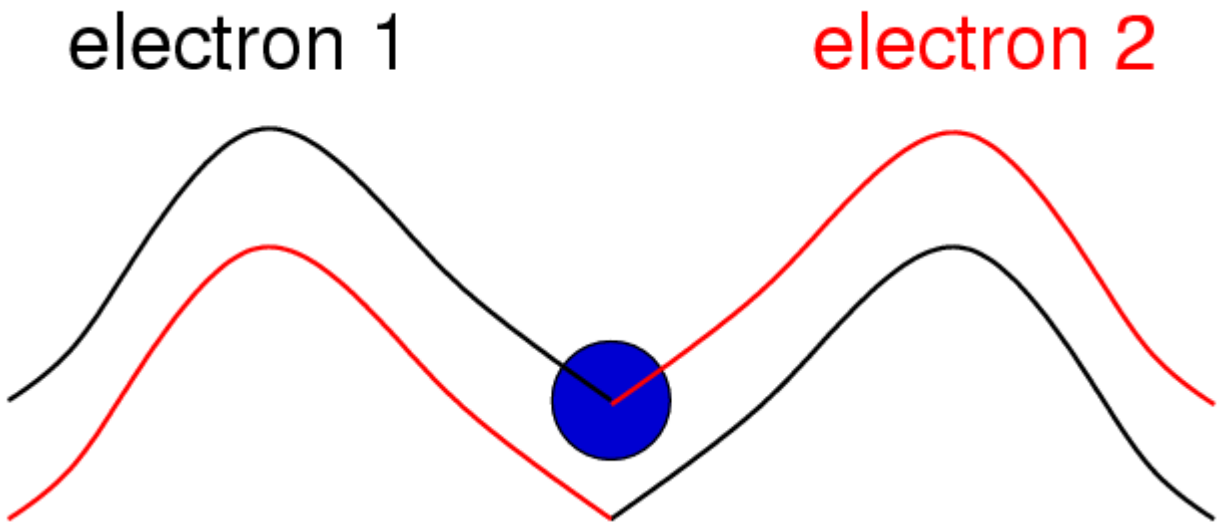
$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ne}}(\mathbf{r}) + V^{\text{Hartree}}(\mathbf{r}) + V^{xc}(\mathbf{r})\right)\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$

Exchange correlation energy

$$V^{xc}(\mathbf{r}) = V^{xc}(\rho(\mathbf{r}), s(\mathbf{r}), \tau(\mathbf{r}))$$

$$\tau(\mathbf{r}) = \sum_n \phi_n^+ \nabla\phi_n,\ s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{3/4}},\ \tau(\mathbf{r}) = \sum_n \phi_n^+ \nabla\phi_n$$

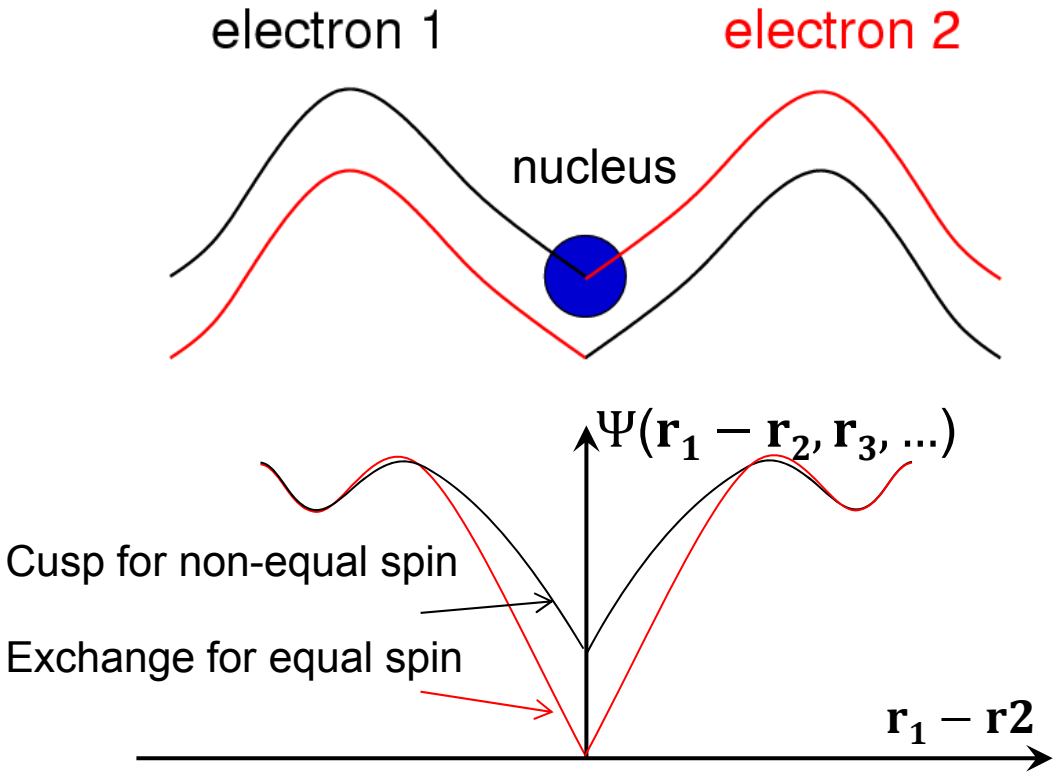
The problem (no free lunch): Correlation

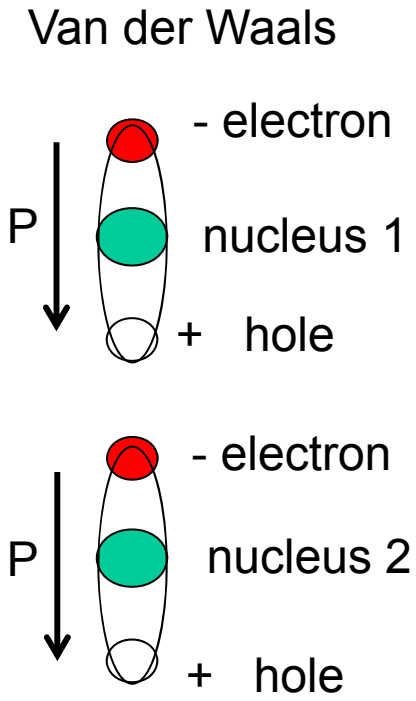


Electrons are correlated, when one electron is to the left the other one will try to avoid this region and move over to the right and vice versa

This is intrinsically non-local and although in principle doable in DFT, it is very difficult to obtain this information from the density alone

The problem of DFT: Correlation





Electrons are correlated, when one electron is to the left the other one will try to avoid this region and move over to the right, and vice versa

This is intrinsically non-local and although DFT should be able to handle this situation, it is very difficult to obtain this information from the density alone

Many body Schrödinger equation

- Schrödinger equation (SE) for molecules or solids

$$\hat{H}\,\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) = E\,\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

- Hamiltonian operator on many-body wave function

$$\hat{H} = \underbrace{-\sum_i \frac{\nabla_i^2}{2}}_{\hat{T}} + \underbrace{\sum_i V_{ne}(\mathbf{x}_i)}_{\hat{V}_{\mathrm{ne}}} + \underbrace{\sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_{\mathrm{ee}}}$$

- Hartree-Fock: single determinant product Ansatz

- Insert into SE and average $\hat{V}_{\mathrm{ee}}$ over all j → Hartree-Fock

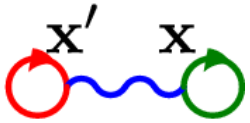
$$\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) \approx \mathcal{A}\,\psi_1(\mathbf{x}_1)\cdot\ldots\cdot\psi_N(\mathbf{x}_N)$$

Hartree-Fock approximation

- *N* electron coupled equations in one variable:

$$(\hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{eff}})\,\psi_i = \varepsilon_i\,\psi_i \qquad \text{with}$$

$$\hat{V}_{\text{eff}}\,\psi_i(\mathbf{x}) = \sum_j \int \mathrm{d}^3\mathbf{x}'\,\frac{\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}')\psi_i^*(\mathbf{x})}{|\mathbf{r}-\mathbf{r}'|}\,\psi_i(\mathbf{x})$$



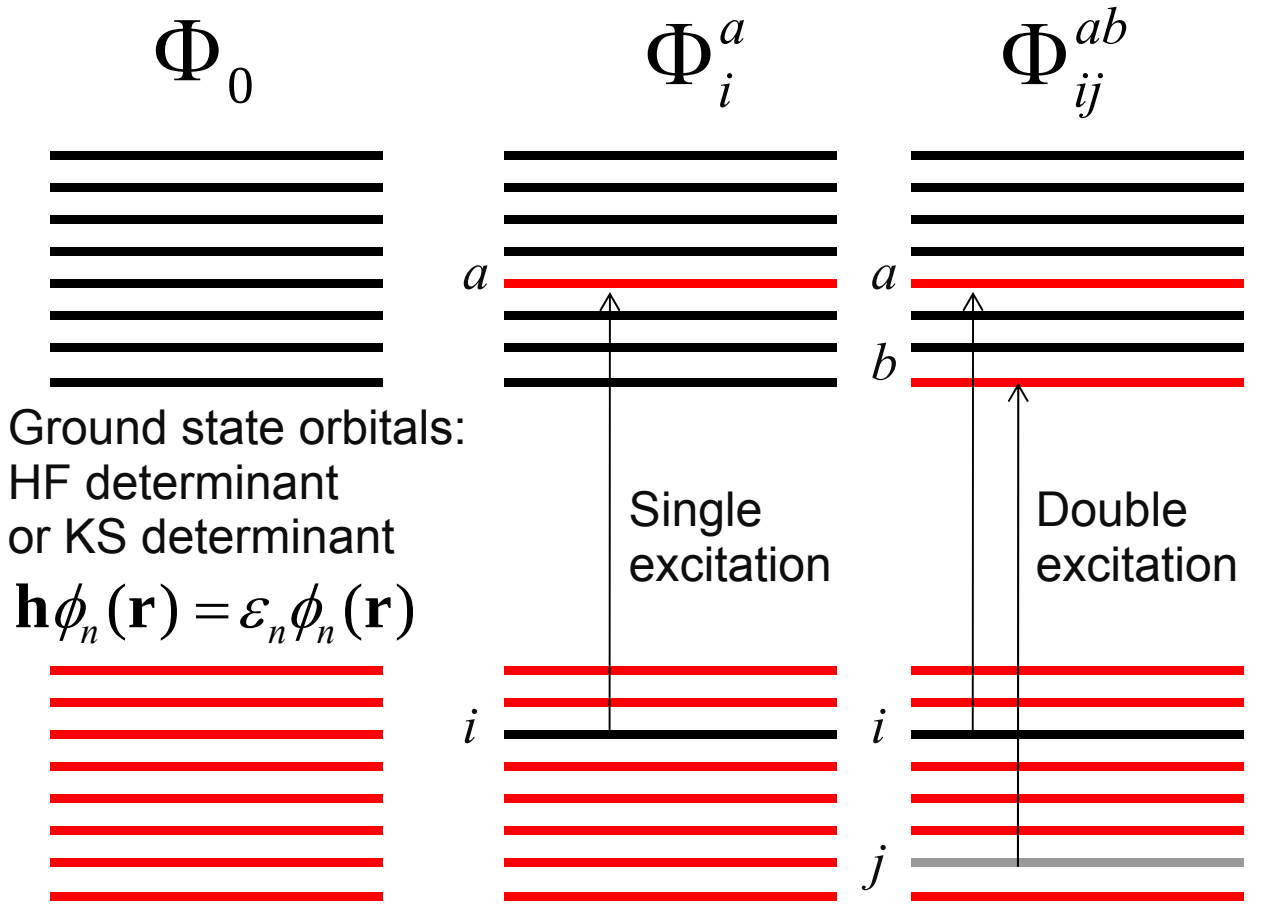
$$- \sum_j \int \mathrm{d}^3\mathbf{x}'\,\frac{\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x})\psi_i^*(\mathbf{x})}{|\mathbf{r}-\mathbf{r}'|}\,\psi_i(\mathbf{x}')$$

- $\hat{V}_{\text{eff}}$ depends on orbitals: solve self-consistently
- HF is variational: true groundstate energy is lower
  the difference is defined as *correlation energy*
- in DFT: $\hat{V}_{\text{eff}}$ is a local potential and a functional of density only
  (and not orbitals)

Many-body perturbation theory

- True many-body wave function can be expanded in terms of reference (HF/DFT) orbitals
- Single reference (discussed here)
  - Using one set of orbitals (Slater determinant, SD)
  - This captures mostly "*dynamic*" correlation or fluctuations (quantum chemistry jargon)
- Multi reference:
  - e.g. at transition states convergence starting from one SD is slow
  - expand in multiple SDs
  - This captures also *static* correlation

Quantum Chemistry methods: CI expansion



Converges slowly with number of excitations

Not size extensive, if truncated

Scales combinatorial

32 orbitals/ 8 elect.

$$\binom{32}{8} \approx 10^{26}$$

coefficients

$$\Phi(r_1, r_2, r_3, \ldots) = \Phi_0 + \sum_{i,a} T_i^a \Phi_i^a + \sum_{ij,ab} T_{ij}^{ab} \Phi_{ij}^{ab} + \ldots$$

Second quantization

- Creation operator: adds states on right column of SD:

$$\hat{c}_k^\dagger \mid \rangle = \begin{vmatrix} \psi_k(\mathbf{x}_1) \end{vmatrix}$$

$$\hat{c}_j^\dagger \begin{vmatrix} \psi_k(\mathbf{x}_1) \end{vmatrix} = \begin{vmatrix} \psi_j(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_j(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \end{vmatrix}$$

$$\hat{c}_i^\dagger \begin{vmatrix} \psi_j(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_j(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \end{vmatrix} = \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \\ \psi_i(\mathbf{x}_3) & \psi_j(\mathbf{x}_3) & \psi_k(\mathbf{x}_3) \end{vmatrix}$$

- Acting twice with the creation operator yields always 0

$$\hat{c}_j{}^+ \hat{c}_j{}^+ \psi_0$$

  Takes care that we do not generate two particles in one orbital (Fermions, so occupancies are 1 or 0)

- Interchanging the order, changes the sign

  this is a property of Slater determinants as you might recall (anti-symmetry), hence the operators observe:

$$\hat{c}_i{}^+ \hat{c}_j{}^+ = -\hat{c}_j{}^+ \hat{c}_i{}^+$$

Second quantization: annihilation operator (1)

- Annihilation operator: removes rightmost state in SD

$$\hat{c}_j \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \\ \psi_i(\mathbf{x}_3) & \psi_j(\mathbf{x}_3) & \psi_k(\mathbf{x}_3) \end{vmatrix} = -\hat{c}_j \begin{vmatrix} \psi_j(\mathbf{x}_1) & \psi_i(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_j(\mathbf{x}_2) & \psi_i(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \\ \psi_j(\mathbf{x}_3) & \psi_i(\mathbf{x}_3) & \psi_k(\mathbf{x}_3) \end{vmatrix} = - \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_k(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_k(\mathbf{x}_2) \end{vmatrix}$$

- If required columns need to be brought to left most side and sign changed accordingly

  Remember, swapping two columns in the Slater determinant changes it's sign
  We just discussed this

- So again, interchanging the order, changes the sign

$$\hat{c}_i \hat{c}_j = -\hat{c}_j \hat{c}_i$$

Second quantization (2)

- Rules to concatenate operators (algebra) follow from definition of Slater determinant and previous slides

$$\{\hat{c}_p^\dagger, \hat{c}_q^\dagger\} = 0 \qquad \{\hat{c}_p, \hat{c}_q\} = 0 \qquad \{\hat{c}_p^\dagger, \hat{c}_q\} = \delta_{pq}$$

where $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$

- In chemistry and solid state physics, one replaces the vacuum ground state by the Hartree-Fock N particle ground state:

$$|\Phi\rangle = \prod_i \hat{c}_i^\dagger \,|\,\rangle = \hat{c}_1^\dagger \ldots \hat{c}_N^\dagger \,|\,\rangle$$

$$|\Phi\rangle = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

- Vacuum state (zero electrons): $|\,\rangle$

The Particle/hole picture

- Instead of vacuum state we define the groundstate to be the one occupied by N electron

$$|\Phi\rangle$$

- Index convention:

$i, j, k, \ldots$	hole excitation	occupied in GS of $\hat{H}_0$	$\varepsilon_i < \varepsilon_\mathrm{F}$
$a, b, c, \ldots$	particle excitation	unoccupied in GS of $\hat{H}_0$	$\varepsilon_a > \varepsilon_\mathrm{F}$

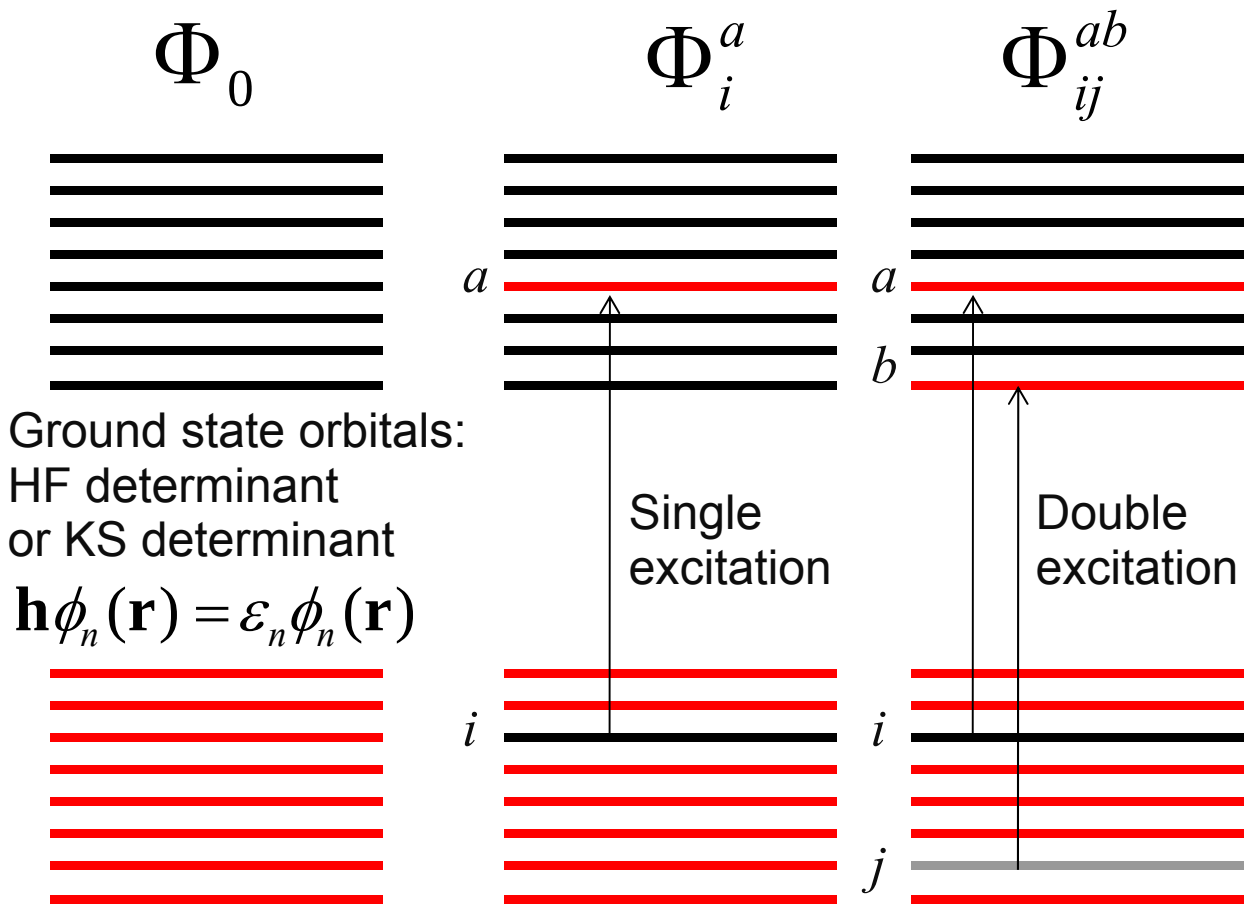
- It is often convenient to introduce Particle/hole **quasiparticle creation/annihilation operators**

$$\hat{a}^\dagger = \hat{c}_a^\dagger \qquad \hat{a} = \hat{c}_a \qquad \text{for} \quad \varepsilon_a > \varepsilon_\mathrm{F}$$
$$\hat{i}^\dagger = \hat{c}_i \qquad \hat{i} = \hat{c}_i^\dagger \qquad \text{for} \quad \varepsilon_i \leq \varepsilon_\mathrm{F}$$

$$\{\hat{i}^\dagger, \hat{j}\} = \delta_{ij} \qquad \{\hat{a}^\dagger, \hat{b}\} = \delta_{ab}$$

- Be careful, do not mix creation/annihilation $\hat{c}_a$, $\hat{c}_i$ and quasiparticle creation/annihilation operators $\hat{a}$, $\hat{\imath}$

Second quantization: Summary



Fermions:

$$\hat{\imath}^+\hat{\imath}^+\Phi_0 = 0$$
$$\hat{a}^+\hat{a}^+\Phi_0 = 0$$

Anticomm. relat.

$$\{\hat{a}, \hat{b}\} = 0$$
$$\{\hat{a}^+, \hat{b}^+\} = 0$$
$$\{\hat{a}^+, \hat{b}\} = \delta_{ab}$$

All intricacies of Fermions are taken care off

Some examples of useful operators

Occupation number operator for state p

$$\hat{N}_p = \hat{c}_p{}^+ \hat{c}_p \qquad \hat{N}_i = \hat{\imath}^+ \hat{\imath} \quad \text{number of holes}$$

Number operator

$$\hat{N} = \sum_p \hat{c}_p{}^+ \hat{c}_p$$

Density matrix operator

$$X_{qp} = \gamma_{qp} = \hat{c}_q{}^+ \hat{c}_p$$

One electron potential

$$\hat{v} = v_q{}^p \;\; \hat{c}_p{}^+ \hat{c}_q$$

For local potential, basis set transformation to real space yields

$$v(\mathbf{r}) \;\; \hat{c}_\mathbf{r}{}^+ \hat{c}_\mathbf{r} = v(\mathbf{r}) \hat{n}_\mathbf{r} \qquad \hat{n}_\mathbf{r} = \hat{c}_\mathbf{r}{}^+ \hat{c}_\mathbf{r}$$

Coulomb operator

Two particle density matrix and Coulomb potential

$$\hat{c}_q{}^+ \hat{c}_p{}^+ \hat{c}_r \hat{c}_s \qquad\qquad \hat{V} = V^{pq}{}_{sr} \;\; \hat{c}_p{}^+ \hat{c}_q{}^+ \hat{c}_r \hat{c}_s$$

To give some feeling what this means, consider

$$\left\langle \Psi | \hat{c}_p{}^+ \hat{c}_q{}^+ \;\hat{c}_r \hat{c}_s | \Psi \right\rangle V^{pq}{}_{sr} = -\left\langle \Psi \left| \hat{c}_p{}^+ \hat{c}_r \, \hat{c}_q{}^+ \hat{c}_s \right| \Psi \right\rangle V^{pq}{}_{sr} + V^{pr}{}_{sr}$$

Basis set transformation from atomic orbitals to real space yields

$$-\left\langle \Psi | \hat{c}_{\mathbf{r}}{}^+ \hat{c}_{\mathbf{r}} \;\hat{c}_{\mathbf{r}'}{}^+ \hat{c}_{\mathbf{r}'} | \Psi \right\rangle \frac{1}{(\mathbf{r} - \mathbf{r}')} = -\left\langle \Psi | \hat{n}_{\mathbf{r}}{}^+ \hat{n}_{\mathbf{r}'} | \Psi \right\rangle \frac{1}{(\mathbf{r} - \mathbf{r}')}$$

Density-density interaction (with particle self-interaction removed)

Again, the density operator in real space is analogous to that in the atomic basis

$$\hat{n}_{\mathbf{r}'} = \hat{c}_{\mathbf{r}'}{}^+ \hat{c}_{\mathbf{r}'}$$

Perturbation Theory

- Hamiltonian split into reference and perturbation part

$$\hat{H} = \underbrace{\hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{eff}}}_{\hat{H}_0} + \underbrace{\hat{V}_{\text{ee}} - \hat{V}_{\text{eff}}}_{\hat{H}_1}$$

- In second quantization

$$\hat{H}_0 = \sum_p \varepsilon_p \hat{c}_p^\dagger \hat{c}_p \qquad \hat{H}_1 = \frac{1}{2} \sum_{pqrs} V_{sr}^{pq} \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s - \sum_{pq} v_q^p \hat{c}_p^\dagger \hat{c}_q$$

with $$V_{sr}^{pq} = \langle pq|\hat{V}_{\text{ee}}|sr\rangle = \iint \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\, \psi_p^*(\mathbf{x})\psi_q^*(\mathbf{x}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_r(\mathbf{x}')\psi_s(\mathbf{x})$$

$$v_q^p = \langle p|\hat{V}_{\text{eff}}|q\rangle = \int \mathrm{d}\mathbf{x}\, \psi_p^*(\mathbf{x}) \left(\hat{V}_{\text{eff}}\psi_q\right)(\mathbf{x})$$

- Reference Hamiltonian is diagonal in its own eigenfunctions
- Usually reference is Hartree-Fock, but DFT is also possible

Interaction picture for time dependent PT

- Split time evolution:
  - operators evolve according to reference $\hat{H}_{1I}(t) = e^{\mathrm{i}\hat{H}_0 t}\hat{H}_1 e^{-\mathrm{i}\hat{H}_0 t}$ (1)
  - states evolve according to perturbation $\mathrm{i}\frac{\partial}{\partial t}|\Psi_I(t)\rangle = \hat{H}_{1I}(t)\,|\Psi_I(t)\rangle$ (2)
- Time evolution operator

$$\hat{U}_I(t,t_0)\,|\Psi_I(t_0)\rangle = |\Psi_I(t)\rangle$$

  - time derivative using (2)

$$\mathrm{i}\frac{\partial}{\partial t}\hat{U}_I(t,t_0)\,|\Psi_I(t_0)\rangle = \hat{H}_{1I}(t)\hat{U}_I(t,t_0)\,|\Psi_I(t_0)\rangle$$

  - integrate

$$\hat{U}_I(t,t_0) = 1 - \mathrm{i}\int_{t_0}^{t} \mathrm{d}t'\,\hat{H}_{1I}(t')\hat{U}_I(t',t_0)$$

  - iterate

$$\begin{aligned}\hat{U}_I(t,t_0) &= 1 - \mathrm{i}\int_{t_0}^{t}\mathrm{d}t'\,\hat{H}_{1I}(t') + \mathrm{i}^2\int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''\,\hat{H}_{1I}(t')\hat{H}_{1I}(t'') - \mathrm{i}^3\ldots \\ &= \sum_{n=0}^{\infty}(-\mathrm{i})^n \int_{t>t_1>\ldots>t_n>t_0} \mathrm{d}t_1\ldots\mathrm{d}t_n\,\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n)\end{aligned}$$

Gell-Man – Low theorem (1)

- Perturbation is slowly turned on from $t=-\infty$ to 0

$$\hat{H}_1(t) = e^{\mathrm{i}\hat{H}_0 t} e^{\eta t} \hat{H}_1 e^{-\mathrm{i}\hat{H}_0 t}$$

- $\eta > 0$ but small, system in groundstate (GS) at any time t
- GS of reference evolves into GS of interacting system

$$|\Psi\rangle = \hat{U}_\eta(0, -\infty)\,|\Phi\rangle$$

  - insert into SE $\quad (\hat{H}_0 + \hat{H}_1)\,|\Psi\rangle = (E_0 + \Delta E)\,|\Psi\rangle$
  - and project onto GS of reference:

$$\begin{aligned} E_0 + \Delta E &= \frac{\langle\Phi|\hat{H}_0|\Psi\rangle}{\langle\Phi\,|\Psi\rangle} + \frac{\langle\Phi|\hat{H}_1|\Psi\rangle}{\langle\Phi\,|\Psi\rangle} \\ &= \frac{\langle\Phi|\hat{H}_0\hat{U}_\eta(0,-\infty)|\Phi\rangle}{\langle\Phi|\hat{U}_\eta(0,-\infty)|\Phi\rangle} + \frac{\langle\Phi|\hat{H}_1(0)\hat{U}_\eta(0,-\infty)|\Phi\rangle}{\langle\Phi|\hat{U}_\eta(0,-\infty)|\Phi\rangle} \end{aligned}$$

Gell-Man – Low theorem (2)

- Correlation energy can be written as vacuum expectation value (VEV) of reference state (HF/DFT):

$$
\begin{aligned}
E_0 + \Delta E &= \frac{\langle \Phi | \hat{H}_0 | \Psi \rangle}{\langle \Phi | \Psi \rangle} + \frac{\langle \Phi | \hat{H}_1 | \Psi \rangle}{\langle \Phi | \Psi \rangle} \\
&= \frac{\langle \Phi | \hat{H}_0 \hat{U}_\eta(0, -\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0, -\infty) | \Phi \rangle} + \frac{\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0, -\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0, -\infty) | \Phi \rangle}
\end{aligned}
$$

- Time evolution operator contains infinite sum and integrals:

$$
\hat{U}_\eta(t, t_0) = \sum_{n=0}^{\infty} (-\mathrm{i})^n \int_{t > t_1 > \ldots > t_n > t_0} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \hat{H}_1(t_1) \ldots \hat{H}_1(t_n)
$$

  - All operators in the interaction picture, I omitted from now

- Nice, however, recipe needed to evaluate VEV

Wick's theorem (1)

- Normal ordering operator reorders into normal order
  Normal order: all creation operators are to the right and all annihilation operators are to the left

$$N[\hat{p}\hat{q}^\dagger] = -\hat{q}^\dagger\hat{p}$$

- The sign is given by the number of required permutations p and is -1^p

- The great thing: VEV of normal ordered operators vanishes

$$\langle\Phi|\hat{A}\hat{B}|\Phi\rangle = \langle\Phi|\hat{A}\hat{B}|\Phi\rangle - \underbrace{\langle\Phi|N[\hat{A}\hat{B}]|\Phi\rangle}_{=0} = \langle\Phi|\hat{A}\hat{B} - N[\hat{A}\hat{B}]|\Phi\rangle =: \langle\Phi|\overbrace{\hat{A}\hat{B}}|\Phi\rangle$$

- This makes live reasonably easy

Wick's theorem: contraction (2)

- ***Contraction*** **= difference between arbitrary and normal order**

$$\overbracket{\hat{A}\hat{B}} := \hat{A}\hat{B} - N[\hat{A}\hat{B}]$$

  - The contraction is always a scalar (and very often zero ☺)

$$\overbracket{\hat{p}\hat{q}} = 0 \qquad \overbracket{\hat{p}\hat{q}^\dagger} = \hat{p}\hat{q}^\dagger - (-\hat{q}^\dagger\hat{p}) = \delta_{pq} \qquad \overbracket{\hat{p}^\dagger\hat{q}} = 0 \qquad \overbracket{\hat{p}^\dagger\hat{q}^\dagger} = 0$$

  - **Contraction only yields a finite value if the annihilation operator is to the left and creation operator is to the right**

$$\overbracket{\hat{p}\hat{q}^\dagger} = \hat{p}\hat{q}^\dagger - (-\hat{q}^\dagger\hat{p}) = \delta_{pq}$$

  - Since contractions are scalars, they can be also placed into the normal ordering operator, and moved around:

$$\hat{A}\hat{B} = N[\hat{A}\hat{B}] + \overbracket{\hat{A}\hat{B}} = N[\hat{A}\hat{B} + \overbracket{\hat{A}\hat{B}}]$$

  - **The normal order is defined for the quasiparticle operators**

Wick's theorem (3): Full contractions

- Extended to more than two operators:

$$\hat{A}\hat{B}\hat{C}\ldots = N\left[\hat{A}\hat{B}\hat{C}\ldots + \text{all possible contractions of } \hat{A}\hat{B}\hat{C}\ldots\right]$$

- e.g. with 4 operators

$$\begin{aligned}\hat{A}\hat{B}\hat{C}\hat{D} \;=\; & N[\hat{A}\hat{B}\hat{C}\hat{D}] + N[\overbrace{\hat{A}\hat{B}}\hat{C}\hat{D}] + N[\overbrace{\hat{A}\hat{B}\hat{C}}\hat{D}] + N[\overbrace{\hat{A}\hat{B}\hat{C}\hat{D}}] + N[\hat{A}\overbrace{\hat{B}\hat{C}}\hat{D}] + \\ & N[\overbrace{\hat{A}\hat{B}\hat{C}\hat{D}}] + N[\hat{A}\overbrace{\hat{B}\hat{C}}\hat{D}] + N[\overbrace{\hat{A}}\hat{B}\overbrace{\hat{C}}\hat{D}] + N[\overbrace{\hat{A}\hat{B}\hat{C}\hat{D}}] + N[\hat{A}\overbrace{\hat{B}\hat{C}\hat{D}}]\end{aligned}$$

- Contractions are numbers; can be pulled out of product:

$$N[\overbrace{\hat{A}\hat{B}\hat{C}}\hat{D}] = -\overbrace{\hat{A}\hat{C}} \times N[\hat{B}\hat{D}]$$

- For a VEV, only fully contracted terms survive

$$\langle\Phi|\hat{A}\hat{B}\hat{C}\hat{D}|\Phi\rangle = \overbrace{\hat{A}\hat{B}}\overbrace{\hat{C}\hat{D}} - \overbrace{\hat{A}\hat{C}}\overbrace{\hat{B}\hat{D}} + \overbrace{\hat{A}\hat{D}}\overbrace{\hat{B}\hat{C}}$$

Wick's theorem applied: 1st order PT

Energy contains term $\frac{\langle\Phi|\hat{H}_1(0)\hat{U}_\eta(0,-\infty)|\Phi\rangle}{\langle\Phi|\hat{U}_\eta(0,-\infty)|\Phi\rangle}$ evaluate for $\hat{U}=1$

- Let us consider only Coulomb term for now:

$$\hat{H}_1(0)=\frac{1}{2}\sum_{pqrs}V_{sr}^{pq}\hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s$$

- 4 operators: $\langle\Phi|\hat{A}\hat{B}\hat{C}\hat{D}|\Phi\rangle=\hat{A}\hat{B}\hat{C}\hat{D}-\hat{A}\hat{C}\hat{B}\hat{D}+\hat{A}\hat{D}\hat{B}\hat{C}$
- contractions: $\hat{p}\hat{q}=0\qquad\hat{p}\hat{q}^\dagger=\hat{p}\hat{q}^\dagger-(-\hat{q}^\dagger\hat{p})=\delta_{pq}\qquad\hat{p}^\dagger\hat{q}=0\qquad\hat{p}^\dagger\hat{q}^\dagger=0$
- only non-vanishing: annihilation to left and same creation to right
- the right operator, must be hole-creation operators: $\hat{i}^\dagger=\hat{c}_i$
- so:

$$\langle\Phi|\hat{H}_1(0)|\Phi\rangle=\frac{1}{2}\sum_{ijkl}V_{lk}^{ij}\hat{i}\hat{j}\hat{k}^\dagger\hat{l}^\dagger+\frac{1}{2}\sum_{ijkl}V_{lk}^{ij}\hat{i}\hat{j}\hat{k}^\dagger\hat{l}^\dagger=-\frac{1}{2}\sum_{ij}V_{ji}^{ij}+\frac{1}{2}\sum_{ij}V_{ij}^{ij}$$

- We will see later, that this can be obtained by simpler reasoning but anyhow, this derivation is exact

2nd order PT: Time dependent operators

- VEVs in Gell-Man – Low theorem:

$$E_0 + \Delta E = \frac{\langle\Phi|\hat{H}_0\hat{U}_\eta(0,-\infty)|\Phi\rangle}{\langle\Phi|\hat{U}_\eta(0,-\infty)|\Phi\rangle} + \frac{\langle\Phi|\hat{H}_1(0)\hat{U}_\eta(0,-\infty)|\Phi\rangle}{\langle\Phi|\hat{U}_\eta(0,-\infty)|\Phi\rangle}$$

$$\hat{U}_\eta(t,t_0) = \sum_{n=0}^{\infty}(-\mathrm{i})^n \int\limits_{t>t_1>\ldots>t_n>t_0} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \hat{H}_1(t_1)\ldots\hat{H}_1(t_n)$$

- Perturbation applied at time t:

$$\hat{H}_1(t) = e^{\mathrm{i}\hat{H}_0 t} e^{\eta t} \frac{1}{2} \sum_{pqrs} V_{sr}^{pq} \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s e^{-\mathrm{i}\hat{H}_0 t}$$

  - insert

$$e^{\pm\mathrm{i}\hat{H}_0 t} = \sum_{p'} |p'\rangle \langle p'| \, e^{\pm\mathrm{i}\varepsilon_{p'} t}$$

  - All states except for p,q,r,s are encountered in both exponents $e^{\pm\mathrm{i}\hat{H}_0 t}$:

$$\hat{H}_1(t) = e^{\eta t} \frac{1}{2} \sum_{pqrs} V_{sr}^{pq} \underbrace{\left(\hat{c}_p^\dagger e^{\mathrm{i}\varepsilon_p t}\right)}_{=\hat{c}_p^\dagger(t)} \left(\hat{c}_q^\dagger e^{\mathrm{i}\varepsilon_q t}\right) \left(\hat{c}_r e^{-\mathrm{i}\varepsilon_r t}\right) \underbrace{\left(\hat{c}_s e^{-\mathrm{i}\varepsilon_s t}\right)}_{=\hat{c}_s(t)}$$

Wick's theorem applied: second order (1)

- Second order: $\langle\Phi|\hat{H}_1(0)\hat{U}_\eta^{(1)}(0,-\infty)|\Phi\rangle$
  - time evolution operator in first order: $\hat{U}_\eta^{(1)}(0,-\infty) = -\mathrm{i}\int_{-\infty}^{0} \mathrm{d}t_1\, \hat{H}_1(t_1)$
  - then perturbation at t=0, where

$$\hat{H}_1(t) = e^{\eta t}\frac{1}{2}\sum_{pqrs} V_{sr}^{pq} \underbrace{\left(\hat{c}_p^\dagger e^{\mathrm{i}\varepsilon_p t}\right)}_{=\hat{c}_p^\dagger(t)} \left(\hat{c}_q^\dagger e^{\mathrm{i}\varepsilon_q t}\right) \left(\hat{c}_r e^{-\mathrm{i}\varepsilon_r t}\right) \underbrace{\left(\hat{c}_s e^{-\mathrm{i}\varepsilon_s t}\right)}_{=\hat{c}_s(t)}$$

$$= \left\langle \Phi \left| -\mathrm{i}\int_{-\infty}^{0} \mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{pqrstuvw} V_{sr}^{pq}V_{wv}^{tu}\, \hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s\hat{c}_t^\dagger(t_1)\hat{c}_u^\dagger(t_1)\hat{c}_v(t_1)\hat{c}_w(t_1) \right| \Phi \right\rangle$$

- Many contractions non-vanishing, one for instance:

$$-\mathrm{i}\int_{-\infty}^{0} \mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{pqrstuvw} V_{sr}^{pq}V_{wv}^{tu}\, \hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s\hat{c}_t^\dagger(t_1)\hat{c}_u^\dagger(t_1)\hat{c}_v(t_1)\hat{c}_w(t_1)$$

$$= -\mathrm{i}\int_{-\infty}^{0} \mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{pqrstuvw} V_{sr}^{pq}V_{wv}^{tu}\, \hat{c}_p^\dagger\hat{c}_w(t_1)\hat{c}_s\hat{c}_t^\dagger(t_1)\hat{c}_q^\dagger\hat{c}_v(t_1)\hat{c}_r\hat{c}_u^\dagger(t_1)$$

Wick's theorem applied: second order (2)

$$-\mathrm{i}\int_{-\infty}^{0}\mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{pqrstuvw} V_{sr}^{pq}V_{wv}^{tu}\,\hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s\hat{c}_t^\dagger(t_1)\hat{c}_u^\dagger(t_1)\hat{c}_v(t_1)\hat{c}_w(t_1)$$

$$= -\mathrm{i}\int_{-\infty}^{0}\mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{pqrstuvw} V_{sr}^{pq}V_{wv}^{tu}\,\hat{c}_p^\dagger\hat{c}_w(t_1)\hat{c}_s\hat{c}_t^\dagger(t_1)\hat{c}_q^\dagger\hat{c}_v(t_1)\hat{c}_r\hat{c}_u^\dagger(t_1)$$

- Contractions reordered to pairs with even number of swaps sign does not change
- Operator order within contraction must not be changed
  - $\hat{c}_p^\dagger\hat{c}_w(t_1)$ creation after annihilation non-zero for holes $p{=}w{=}i$, $q{=}v{=}j$
  - $\hat{c}_s\hat{c}_t^\dagger(t_1)$ annihilation after creation non-zero for particles $s{=}t{=}a$, $r{=}u{=}b$
- Time integration yields energy denominator

$$-\mathrm{i}\int_{-\infty}^{0}\mathrm{d}t_1\, e^{\eta t_1}\frac{1}{4}\sum_{ijab} V_{ab}^{ij}V_{ij}^{ab}\, e^{-\mathrm{i}\varepsilon_i t_1}e^{\mathrm{i}\varepsilon_a t_1}e^{-\mathrm{i}\varepsilon_j t_1}e^{\mathrm{i}\varepsilon_b t_1} = \frac{1}{4}\sum_{ijab}\frac{V_{ab}^{ij}V_{ij}^{ab}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b+\mathrm{i}\eta}$$

Gell-Man – Low theorem & Wick theorem

- Correlation energy can be written as vacuum expectation value (VEV) of reference state (HF/DFT):

$$
\begin{aligned}
E_0 + \Delta E &= \frac{\langle \Phi | \hat{H}_0 | \Psi \rangle}{\langle \Phi | \Psi \rangle} + \frac{\langle \Phi | \hat{H}_1 | \Psi \rangle}{\langle \Phi | \Psi \rangle} \\
&= \frac{\langle \Phi | \hat{H}_0 \hat{U}_\eta(0, -\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0, -\infty) | \Phi \rangle} + \frac{\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0, -\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0, -\infty) | \Phi \rangle}
\end{aligned}
$$

- Time evolution operator contains infinite sum and integrals:

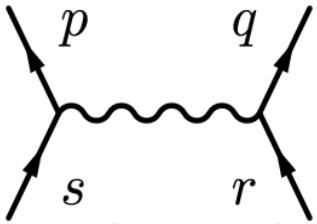
$$
\hat{U}_\eta(t, t_0) = \sum_{n=0}^{\infty} (-\mathrm{i})^n \int_{t > t_1 > \ldots > t_n > t_0} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \hat{H}_1(t_1) \ldots \hat{H}_1(t_n)
$$

- Wick theorem is used to evaluate all encountered vacuum expectation values (VEV)

Goldstone diagrams

- Contractions
  - Pauli principle is exactly observed
  - There are many contractions, tedious to go through all
- Bookkeeping using Goldstone diagrams
  - Coulomb operator → wiggly line with left/right vertex at equal time
  - One-electron potential → dashed blob with incoming/outgoing vertex

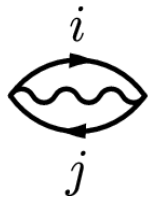
$$V_{sr}^{pq}\hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s =$$



$$v_q^p\hat{c}_p^\dagger\hat{c}_q =$$

  - At each vertex one incoming and one outgoing line
  - For lines that finish and start at same time → sum over occupied states

$$\frac{1}{2}\sum_{ij} V_{ji}^{ij}\hat{i}\hat{j}\hat{i}^\dagger\hat{j}^\dagger =$$

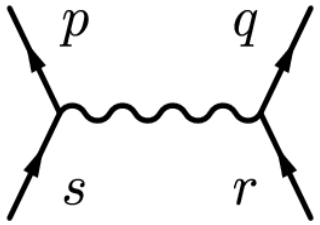


$$\frac{1}{2}\sum_{ij} V_{ij}^{ij}\hat{i}\hat{j}\hat{j}^\dagger\hat{i}^\dagger = i$$

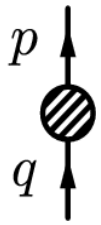
Goldstone diagrams

- Bookkeeping using Goldstone diagrams
  - Coulomb operator and dashed blobs

$$V_{sr}^{pq}\hat{c}_p^\dagger\hat{c}_q^\dagger\hat{c}_r\hat{c}_s =$$



$$v_q^p\hat{c}_p^\dagger\hat{c}_q =$$

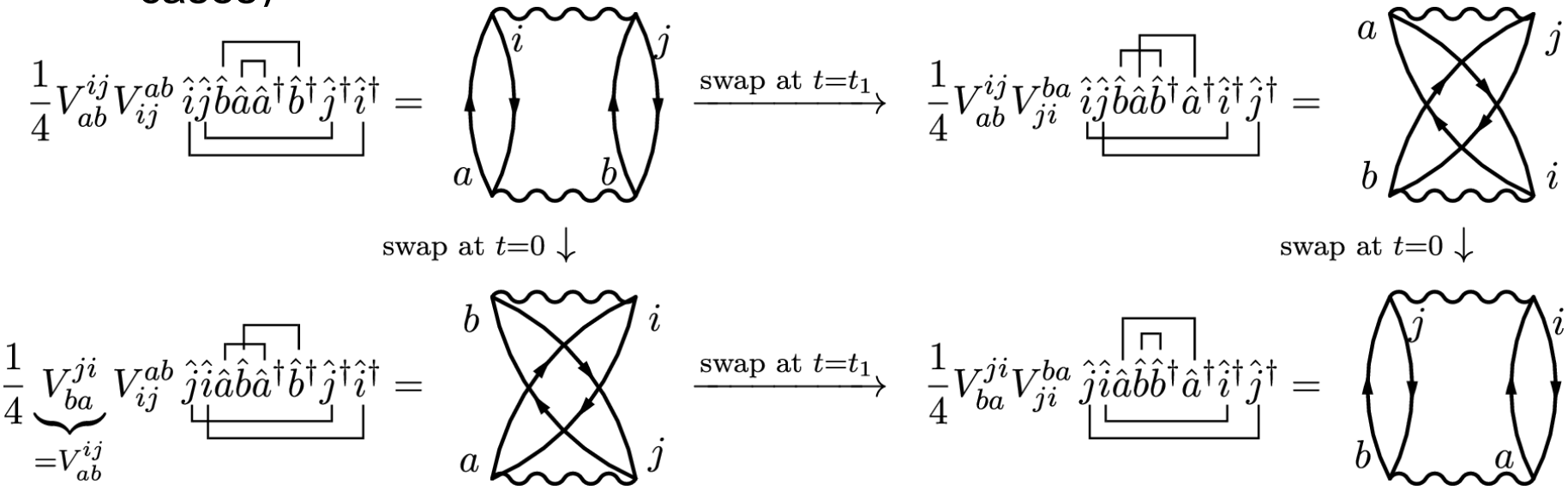


  - Order is given by the number of Coulomb line + dashed blobs
  - Essentially draw all conceivable closed diagrams with n Coulomb lines & dashed blobs (Coulomb is always horizontal; equal time)
  - Then there are simple rules to convert the diagram to an algebraic equation
  - Specifically rules for
    - Pre-factors (related to symmetry)
    - Denominator (coming from integration over time)
    - Sign

Goldstone diagrams – pre-factors symmetries

Swapping left/right vertices of Coulomb interaction, yields the same Goldstone diagram (symmetry of Coulomb interaction)

- Interchange, generally corresponds to a distinct contractions (left two cases)



- All 2^n contractions from interchanging the left/right vertex in the Coulomb operator cancel the factor $(½)^n$ from Coulomb operators
- However, if the *entire* diagram has left/right symmetry, a factor ½ prevails (only half of the contractions are distinct)

Goldstone diagrams – time integration (1)

- Time evolution operator has a specific time order

$$\hat{U}_\eta(t,t_0) = \sum_{n=0}^{\infty}(-\mathrm{i})^n \int_{t>t_1>\ldots>t_n>t_0} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \hat{H}_1(t_1)\ldots\hat{H}_1(t_n)$$

- Transform to time differences between two interactions:

$$\begin{aligned}
t_{0,1} &= 0 - t_1 \\
t_{1,2} &= t_1 - t_2 \\
&\vdots \qquad\qquad \ddots \\
t_{n-1,n} &= t_{n-1} - t_n
\end{aligned}$$

  - so $0 - t_n = t_{0,1} + t_{1,2} + \ldots + t_{n-1,n}$
  - for state a created at t_n and annihilated at 0 the phase factor is

$$e^{-\varepsilon_a 0}\ldots e^{\varepsilon_a t_n} = e^{-\varepsilon_a t_{0,1}} e^{-\varepsilon_a t_{1,2}} \ldots e^{-\varepsilon_a t_{n-1,n}}$$

- Energy of state a occurs in the exponent of every time interval in which the state propagates

Goldstone diagrams – time integration (2)

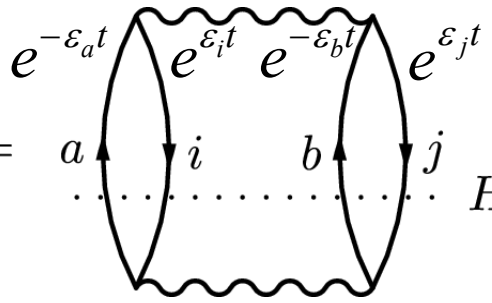
- Integrating each interval from 0 to ∞ yields an energy denominator for *k*-th interval (counted from top):

$$\frac{1}{\sum_{i\in H_k}\varepsilon_i - \sum_{a\in P_k}\varepsilon_a + ki\eta}$$

  - sum of hole states – sum of particle states in that time interval
  - small imaginary part from slowly turning perturbation on

- e.g. MP2 direct diagram:

$$\frac{1}{2}\sum_{ijab}\frac{V_{ab}^{ij}V_{ij}^{ab}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b+\mathrm{i}\eta} =$$



$H = \{i, j\}, P = \{a, b\}$

  - factor ½ from left/right symmetry of diagram

Goldstone diagrams – Fermion sign

- Ordering contracted operators in pairs using *P* swaps:

$$\hat{A}\hat{B}\hat{C}\ldots\hat{Z} = (-1)^P \hat{A}\hat{C}\hat{B}\hat{Z}\ldots$$

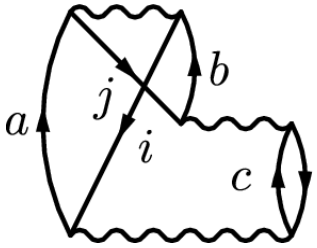
  - same sign for all 2^n contractions of one Goldstone diagram

  - sign can be determined from topology and is give by

$$(-1)^{l+h}$$

  - l … number of closed loops in Fermion connections,
  - h … number of hole lines

- e.g.: third order diagram:



$$= (-1)^{2+3} \sum_{ijkabc} \frac{V_{ik}^{ac} V_{jc}^{bk} V_{ab}^{ji}}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)}$$

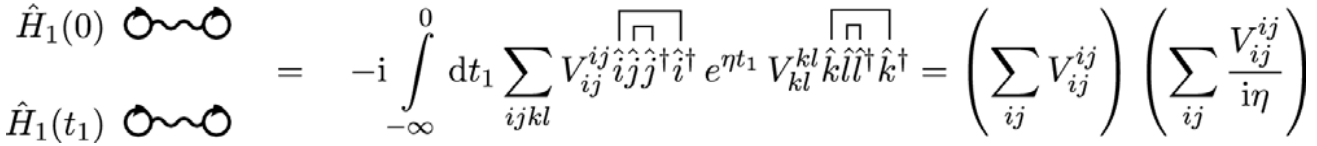
(2 loops, 3 holes, no left/right symmetry of whole diagram)

Linked cluster theorem (1)

- VEVs in Gell-Man – Low theorem:

$$E_0 + \Delta E = \frac{\langle \Phi | \hat{H}_0 \hat{U}_\eta(0,-\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0,-\infty) | \Phi \rangle} + \frac{\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0,-\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0,-\infty) | \Phi \rangle}$$

  - Diagram is *disconnected* , if diagram is not connected to last $H_1(0)$:



  - disconnected parts separate into independent factors, so:

$$\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0,-\infty) | \Phi \rangle = \left(\sum \text{connected diagrams} \right) \left(\sum \text{disconnected diagrams} \right)$$

  - numerator containing $\hat{H}_0 = E_0 - \sum_i \varepsilon_i \hat{i}^\dagger \hat{i} + \sum_a \varepsilon_a \hat{a}^\dagger \hat{a}$

$$\langle \Phi | \hat{H}_0 \hat{U}_\eta(0,-\infty) | \Phi \rangle = E_0 \left(\sum \text{disconnected diagrams} \right)$$

Linked cluster theorem (2)

- VEVs in Gell-Man – Low theorem:

$$E_0 + \Delta E = \frac{\langle \Phi | \hat{H}_0 \hat{U}_\eta(0,-\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0,-\infty) | \Phi \rangle} + \frac{\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0,-\infty) | \Phi \rangle}{\langle \Phi | \hat{U}_\eta(0,-\infty) | \Phi \rangle}$$

  - numerators:

$$\langle \Phi | \hat{H}_1(0) \hat{U}_\eta(0,-\infty) | \Phi \rangle = \left(\sum \text{connected diagrams} \right) \left(\sum \text{disconnected diagrams} \right)$$

$$\langle \Phi | \hat{H}_0 \hat{U}_\eta(0,-\infty) | \Phi \rangle = E_0 \left(\sum \text{disconnected diagrams} \right)$$

  - denominators, same as numerator without last $H_1(0)$:

$$\langle \Phi | \hat{U}_\eta(0,-\infty) | \Phi \rangle = \left(\sum \text{disconnected diagrams} \right)$$

$t = 0$ ⋯⋯⋯

$\hat{H}_1(t_1)$ 

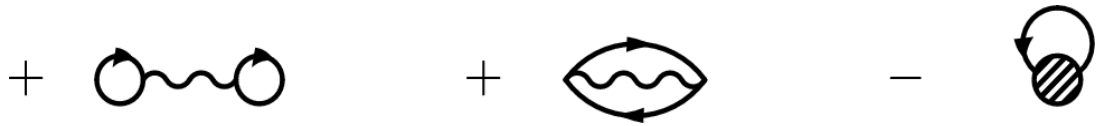
$$= \left(\sum_{ij} \frac{V_{ij}^{ij}}{i\eta} \right)$$

  - (diverging) disconnected diagrams *cancel*

- correlation energy: $\Delta E = \left(\sum \text{connected diagrams} \right)$

Hartree-Fock reference (1)

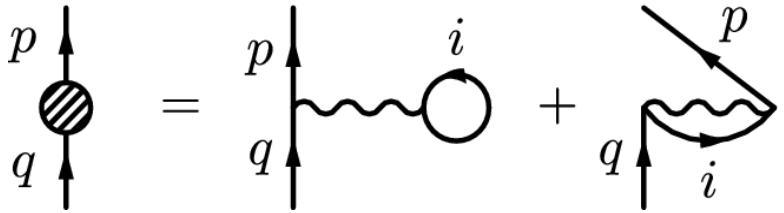
- Inclusion of effective interaction; in first order:



  - effective interaction is subtracted in H_1

- Effective interaction in Hartree-Fock:

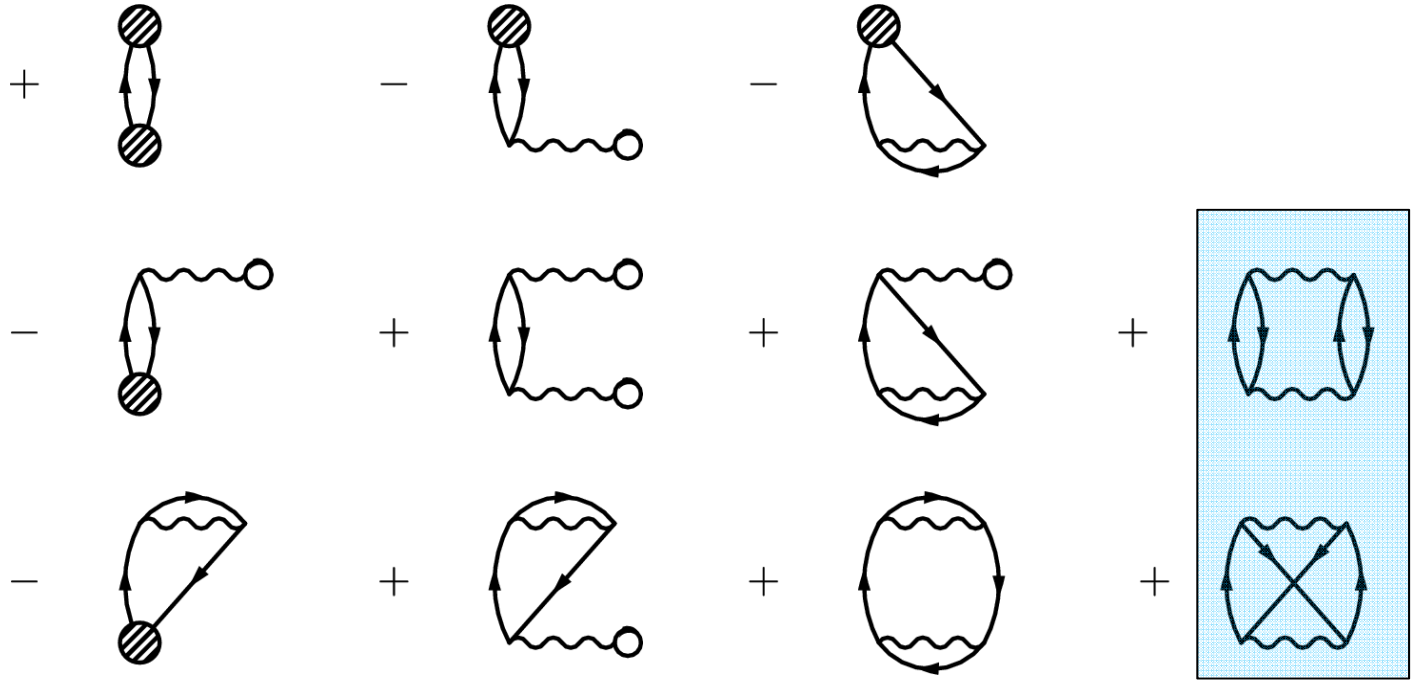
$$v_q^p \hat{c}_p^\dagger \hat{c}_q = \sum_i V_{qi}^{pi} \hat{c}_p^\dagger \hat{c}_q - \sum_i V_{qi}^{ip} \hat{c}_p^\dagger \hat{c}_q$$



- First order term is therefore zero in HF:

Hartree-Fock reference (2)

- In 2nd order already 11 diagrams containing $\hat{V}_{eff}$:



  - sign from $\hat{V}_{eff}$ is given explicitly, sign related to topology not
  - in HF: $\hat{V}_{eff}$ cancels all 9 diagrams containing non-propagating connections (on the same Coulomb line), only MP2 remains
- In DFT diagrams need to be included

Propagators (1)

- Evaluating Goldstone diagrams requires Coulomb matrix

$$V_{sr}^{pq} = \iint \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\,\psi_p^*(\mathbf{x})\psi_q^*(\mathbf{x}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_r(\mathbf{x}')\psi_s(\mathbf{x})$$

  - expensive: $O(N^5)$ in time, $O(N^4)$ in memory

- Some diagrams can be evaluated more conveniently, e.g. Hartree

$$= \frac{1}{2}\sum_{ij} V_{ij}^{ij} = \frac{1}{2}\sum_{ij}\iint \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\,\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_j(\mathbf{x}_2)\psi_i(\mathbf{x}_1)$$

$$= \frac{1}{2}\iint \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\left(\sum_i \psi_i^*(\mathbf{x}_1)\psi_i(\mathbf{x}_1)\right)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\left(\sum_i \psi_i^*(\mathbf{x}_2)\psi_i(\mathbf{x}_2)\right)$$

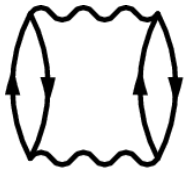
$$= \frac{1}{2}\iint \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\,G_0(\mathbf{x}_1 0,\mathbf{x}_1 0)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}G_0(\mathbf{x}_2 0,\mathbf{x}_2 0)$$

  - G_0 *Green's function* for equal time t = charge density

$$G_0(\mathbf{x}t,\mathbf{x}'t) := -\sum_i \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}')$$

Propagators (2)

- For “connections” propagating in time:



$$= \frac{1}{2}(-\mathrm{i})\int_{-\infty}^{0} \mathrm{d}t \iiiint \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}_3\,\mathrm{d}\mathbf{x}_4 \frac{1}{|\mathbf{r}_1-\mathbf{r}_3|}\frac{1}{|\mathbf{r}_2-\mathbf{r}_4|}$$
$$\underbrace{\sum_j \psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_4)e^{(-\mathrm{i}\varepsilon_j+\eta)t}}_{=-G_0(\mathbf{x}_4 t,\mathbf{x}_2 0)} \underbrace{\sum_b \psi_b(\mathbf{x}_2)\psi_b^*(\mathbf{x}_4)e^{(\mathrm{i}\varepsilon_b+\eta)t}}_{=+G_0(\mathbf{x}_2 0,\mathbf{x}_4 t)}$$
$$\sum_i \psi_i^*(\mathbf{x}_1)\psi_i(\mathbf{x}_3)e^{(-\mathrm{i}\varepsilon_i+\eta)t} \sum_a \psi_a(\mathbf{x}_1)\psi_a^*(\mathbf{x}_3)e^{(\mathrm{i}\varepsilon_a+\eta)t}$$

  - η arbitrarily small, put in time dependent operators

- Define propagator:

$$G_0(\mathbf{x}t,\mathbf{x}'t') := \begin{cases} -\sum_i \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}')e^{(-\mathrm{i}\varepsilon_i+\eta)(t-t')} & \text{for } t \le t' \\ +\sum_a \psi_a(\mathbf{x})\psi_a^*(\mathbf{x}')e^{(-\mathrm{i}\varepsilon_a-\eta)(t-t')} & \text{otherwise.} \end{cases}$$

Feynman diagrams (1)

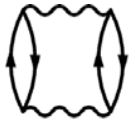
- In Goldstone diagrams time stands out (treated specially)

$$\hat{U}_\eta(t,t_0) = \sum_{n=0}^{\infty}(-\mathrm{i})^n \int_{t>t_1>\ldots>t_n>t_0} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \hat{H}_1(t_1)\ldots\hat{H}_1(t_n)$$

  - equal footing desired, e.g. in frequency domain requiring $\int_{-\infty}^{\infty}\mathrm{d}t_1 \ldots \int_{-\infty}^{\infty}\mathrm{d}t_n$ instead of $\int_{0>t_1>\ldots>t_n}\mathrm{d}t_1\ldots\mathrm{d}t_n$

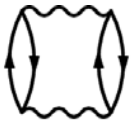
- Example of MP2 direct diagram

  - every H_1 in U introduces time variable & imaginary unit; do the same for last $H_1(0)$:



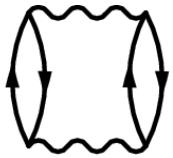
$$(-\mathrm{i}) = \frac{1}{2}\int_{t_1>t_3} \mathrm{d}t_1\mathrm{d}t_3 \iiint \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}_3\,\mathrm{d}\mathbf{x}_4\,\delta(t_1)\,\frac{(-\mathrm{i})}{|\mathbf{r}_1-\mathbf{r}_2|}\,\frac{(-\mathrm{i})}{|\mathbf{r}_3-\mathbf{r}_4|}$$
$$G_0(x_1t_1,x_3t_3)\,G_0(x_3t_3,x_1t_1)\,G_0(x_2t_1,x_4t_3)\,G_0(x_4t_3,x_2t_1)$$

  - drop constraints on integration times, respecting double counting

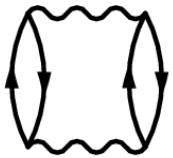


$$(-\mathrm{i}) = \frac{1}{4}\iint_{-\infty}^{\infty} \mathrm{d}t_1\mathrm{d}t_3 \iiint \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}_3\,\mathrm{d}\mathbf{x}_4\,\delta(t_1)\,\frac{(-\mathrm{i})}{|\mathbf{r}_1-\mathbf{r}_2|}\,\frac{(-\mathrm{i})}{|\mathbf{r}_3-\mathbf{r}_4|}$$
$$G_0(x_1t_1,x_3t_3)\,G_0(x_3t_3,x_1t_1)\,G_0(x_2t_1,x_4t_3)\,G_0(x_4t_3,x_2t_1)$$

Feynman diagrams (2)

$$(-\mathrm{i})\ \raisebox{-0.5em}{  }\ = \frac{1}{4}\iint_{-\infty}^{\infty} \mathrm{d}t_1 \mathrm{d}t_3 \iiint\!\!\iint \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}_3\,\mathrm{d}\mathbf{x}_4\,\delta(t_1)\,\frac{(-\mathrm{i})}{|\mathbf{r}_1-\mathbf{r}_2|}\,\frac{(-\mathrm{i})}{|\mathbf{r}_3-\mathbf{r}_4|}$$
$$G_0(x_1t_1,x_3t_3)\,G_0(x_3t_3,x_1t_1)\,G_0(x_2t_1,x_4t_3)\,G_0(x_4t_3,x_2t_1)$$

- Introduce time at every vertex

$$(-\mathrm{i})\ \raisebox{-0.5em}{  }\ = \frac{1}{4}\iiint\!\!\iint_{-\infty}^{\infty} \mathrm{d}t_1\mathrm{d}t_2\mathrm{d}t_3\mathrm{d}t_4 \iiint\!\!\iint \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}_3\,\mathrm{d}\mathbf{x}_4$$
$$G_0(x_1t_1,x_3t_3)\,G_0(x_3t_3,x_1t_1)\,G_0(x_4t_4,x_2t_2)\,G_0(x_2t_2,x_4t_4)$$
$$\delta(t_1)\,\underbrace{\frac{(-\mathrm{i})}{|\mathbf{r}_1-\mathbf{r}_2|}\,\delta(t_1-t_2)}_{=V(\mathbf{x}_1t_1,\mathbf{x}_2t_2)}\,\frac{(-\mathrm{i})}{|\mathbf{r}_3-\mathbf{r}_4|}\,\delta(t_3-t_4)$$

- Define propagator of Coulomb interaction:

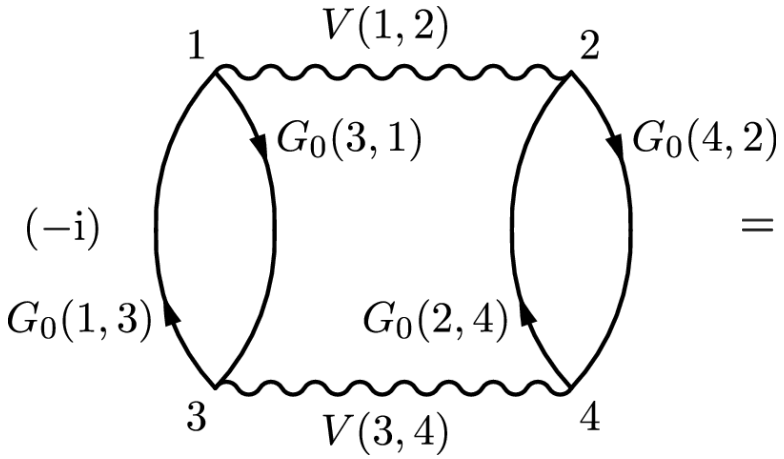
$$V(\mathbf{x}t,\mathbf{x}'t') := \frac{(-\mathrm{i})}{|\mathbf{r}-\mathbf{r}'|}\,\delta(t-t')$$

Feynman diagrams (3)

- Propagators

$$V(\mathbf{x}t, \mathbf{x}'t') := \frac{(-\mathrm{i})}{|\mathbf{r}-\mathbf{r}'|}\,\delta(t-t') \qquad G_0(\mathbf{x}t, \mathbf{x}'t') := \begin{cases} -\sum_i \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}')e^{(-\mathrm{i}\varepsilon_i+\eta)(t-t')} & \text{for } t \le t' \\ +\sum_a \psi_a(\mathbf{x})\psi_a^*(\mathbf{x}')e^{(-\mathrm{i}\varepsilon_a-\eta)(t-t')} & \text{otherwise.} \end{cases}$$

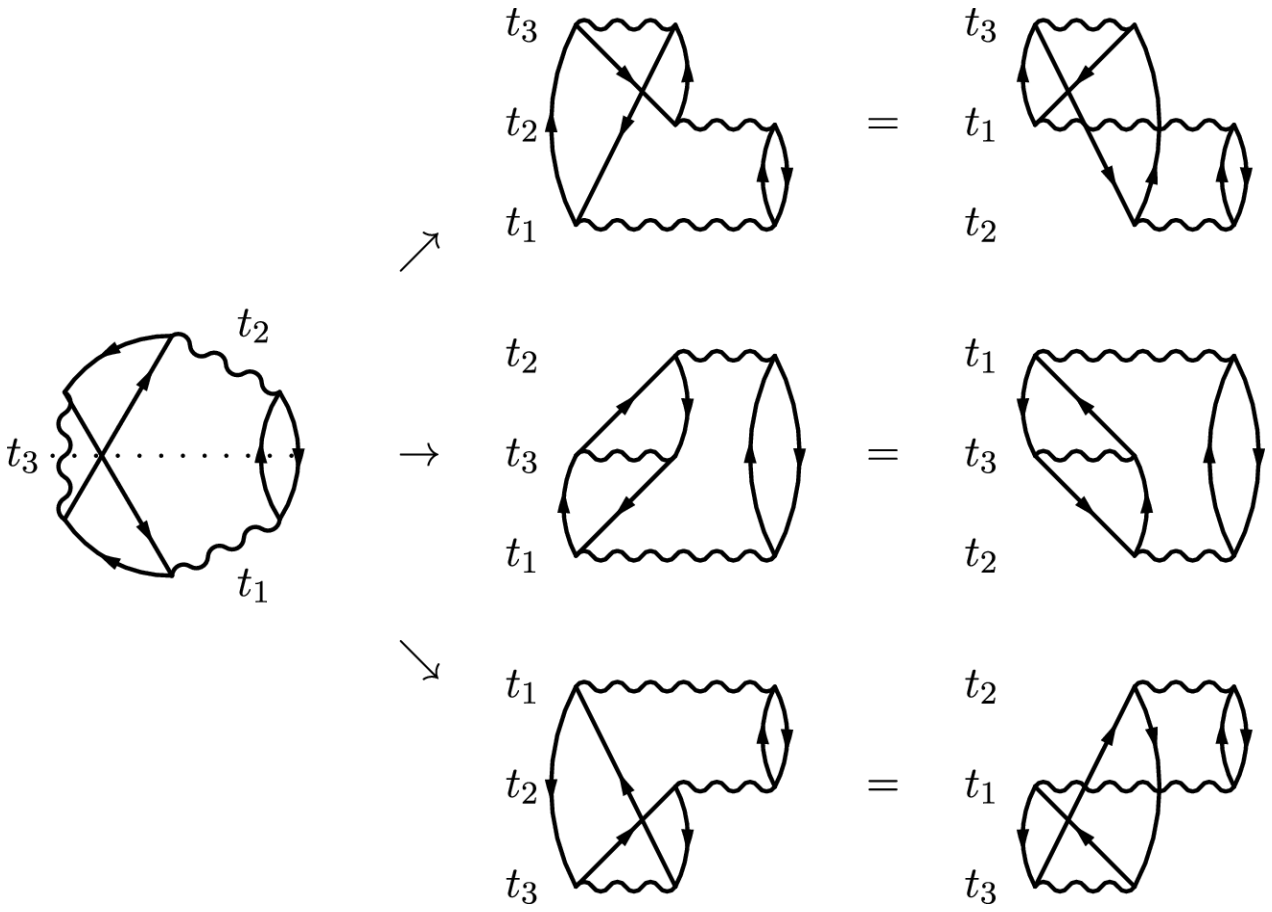
- Fermion sign: $(-1)^l$
  - negative sign of holes contained in propagator
- Evaluate Feynman diagram: integrate all vertex positions & times (note: imaginary unit on lhs, delta on rhs in time domain)



$$= \frac{1}{4}\iiiint \mathrm{d}1\,\mathrm{d}2\,\mathrm{d}3\,\mathrm{d}4\,\delta(t_1)\, G_0(1,3)\,G_0(3,1)\,V(3,4)\,G_0(4,2)\,G_0(2,4)\,V(2,1)$$

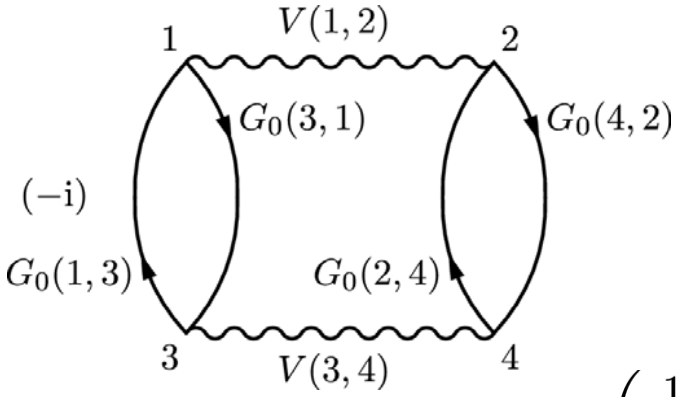
Feynman diagrams – symmetries (1)

- Dropping time order constraints introduces many permutations
  - In general, each permutation leads to a distinct Goldstone diagram
  - Here, only half are distinct due to reflection symmetry



Feynman diagrams – symmetries (2)

- Feynman diagrams allow treatment of symmetries in space & time (left/right symmetries, and time permutation symmetries)
- Find symmetries graphically or computer aided, given vertices: 1,2,3,4
  - undirected set of Bosonic edges (left/right symmetry of Coulomb)
  - directed set of Fermionic edges (particle != hole)



$$B = \{\{1,2\},\{3,4\}\}$$
$$F = \{(1,3),(3,1),(2,4),(4,2)\}$$

  - e.g. permutation $\tau = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 2 & 1 \end{pmatrix}$ leaves sets *B* and *F* invariant:

$$\tau(B) = \{\{4,3\},\{2,1\}\} = B$$
$$\tau(F) = \{(4,2),(2,4),(3,1),(1,3)\} = F$$

- Here, 2 reflection symmetries of order 2 → ¼ of all permutations distinct (called *symmetry factor*)

Many-body PT – Summary

- Recipe for systematic approximation of
  - GS energy of fully interacting system
  - Yields orbitals and eigenenergies of reference (HF/DFT)
- Presented here up to second order
  - finite order based on HF is also termed *Møller – Plesset PT*
- Pros
  - extensive $E(N \text{ atoms}) = N\,E(\text{atom})$ in same chemical environment
  - quickly convergent for insulators MP3, MP4
- Cons
  - slowly convergent with respect to number of virtual orbitals *a*
  - not variational: no upper bound for energy, forces difficult
  - still infinite number of diagrams, *n*! with growing order *n*

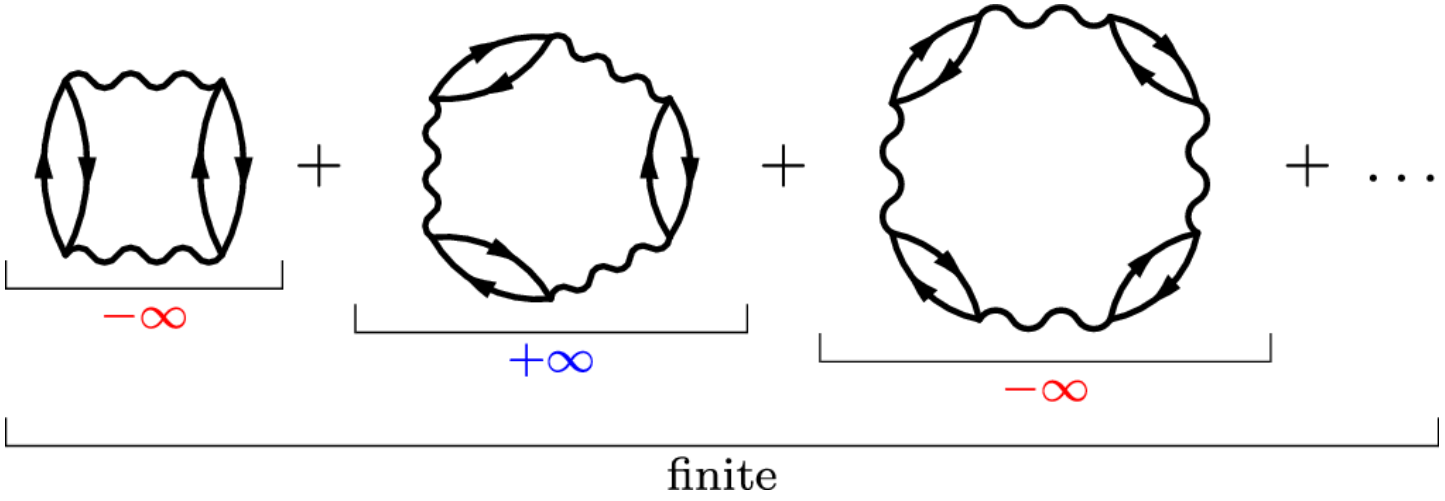
Goldstone VS. Feynman diagrams

property	Goldstone	Feynman
Coulomb lines	parallel (horizontal)	only topology matters
Moving vertices	horizontally only	move at will
Contains (in general)	2^n contractions	$n!$ Goldstone diagrams
Evaluation	contract Coulomb tensors	integrate complex functions
Symmetries	space only (½)	space & time
Relativistic treatment	Scalar relativistic + SO	relativistic propagators
Frequency domain	N.A.	by Fourier transform
Access to last interaction	yes	N.A.

- Access to last interaction allows Goldstone diagrams to be used for iterative construction of more complex diagrams

Application: direct ring Coupled Cluster Doubles

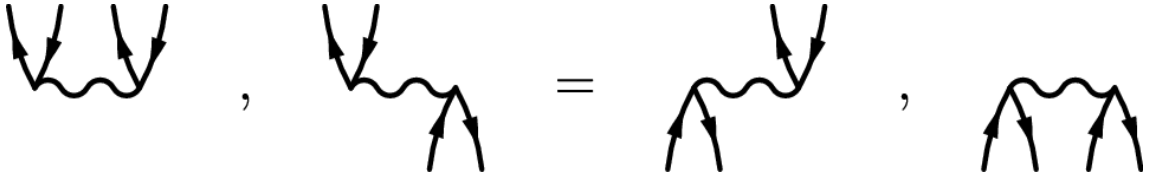
- Finite order PT not applicable to metals
  ring diagrams diverge:

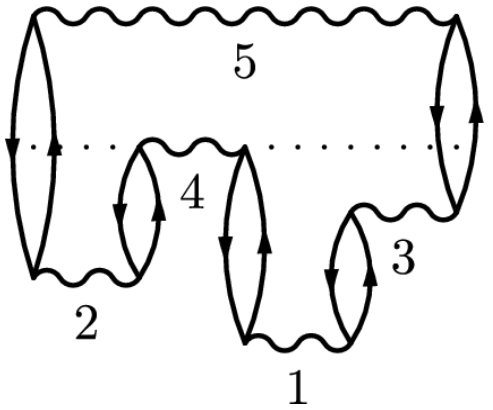


- (Macke 1950) a student of Heisenberg found
  - sum states then orders: -infinity + infinity - infinity …
  - sum orders then states: finite (and reasonable) result
  - called *renormalization* in QFT
  - sum over *all* ring diagrams called *Random Phase Approximation*

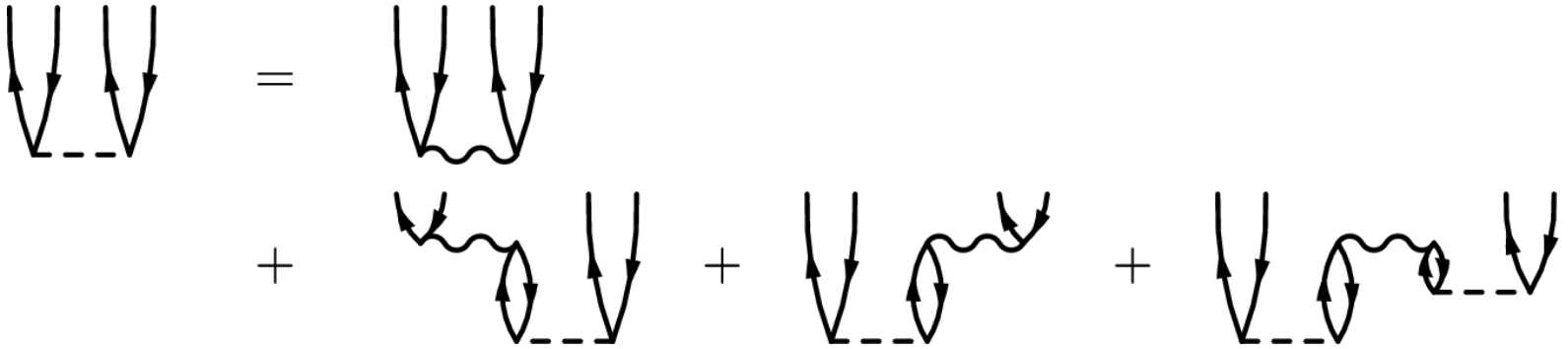
drCCD amplitudes (1)

- 4 case of interaction occur in a ring:



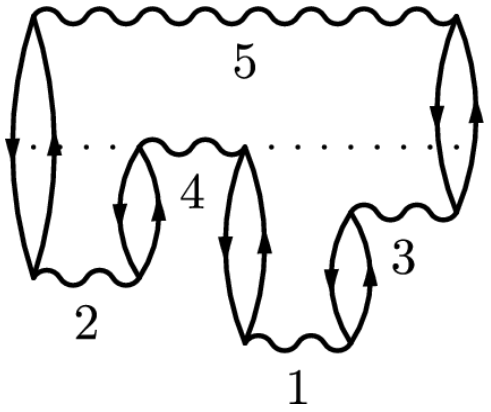


- (Freeman 1977) ring diagrams from drCCD amplitudes

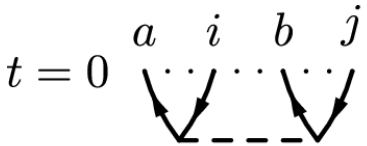


  - every way to end up with two particle/hole pairs using only bubbles (recursive definition)
  - build ring from bottom to top, following left/right particle/hole pair (access to last interaction needed, using Goldstone diagrams)

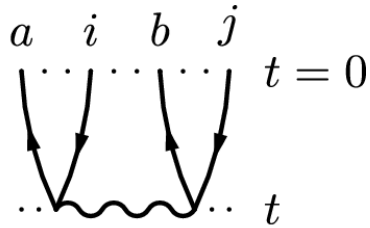
drCCD amplitudes (2)



- 1st case, found in interaction 1 & 2
  - Coulomb interaction creates new particle/hole pair
  - probability amplitudes of finding two pairs in state *a,i* and *b,j* stored in 4 point tensor
  - amplitudes for *t*=0
  - Coulomb interaction can occur at any time *t*<0:



$$t_{ij}^{ab} = (-\mathrm{i}) \int_{-\infty}^{0} \mathrm{d}t\, e^{\eta t}\, e^{\varepsilon_a t}\, e^{\varepsilon_b t}\, e^{-\varepsilon_i t}\, e^{-\varepsilon_j t}\, V_{ij}^{ab} + \ldots$$

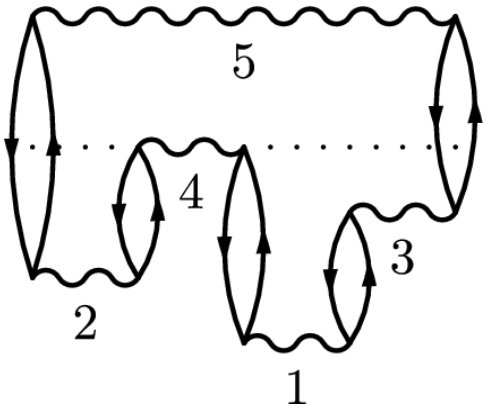


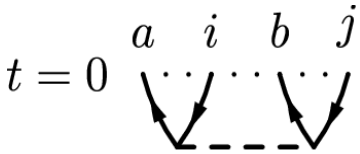
$$= \frac{V_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b + \mathrm{i}\eta} + \ldots$$

  - further cases to come ...

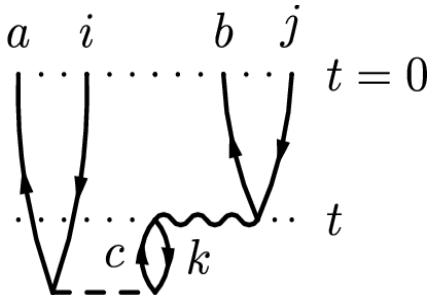
drCCD amplitudes (3)

- 2nd case, found in interaction 3
  - right particle/hole pair contracted with interaction, creating new particle/hole pair
  - interaction occurred at any time t<0
  - contraction with amplitudes at that time (recursive usage of amplitudes)





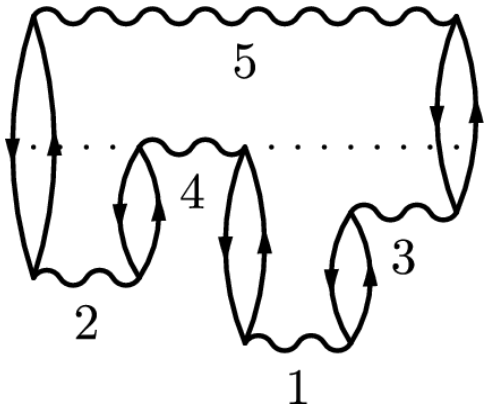
$$t_{ij}^{ab} = \ldots + \frac{\sum_{kc} t_{ik}^{ac} V_{cj}^{kb}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b + \mathrm{i}\eta} + \ldots$$

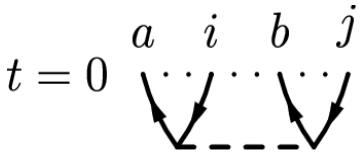


  - one more loop, one more hole gives positive Fermion sign
  - more cases to come ...

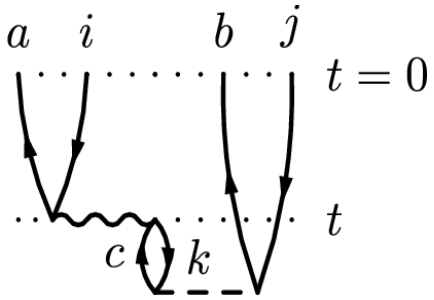
drCCD amplitudes (4)

- 3rd case, mirrored case of interaction 3
  - left particle/hole pair contracted with interaction, creating new particle/hole pair
  - analogous to 2nd case



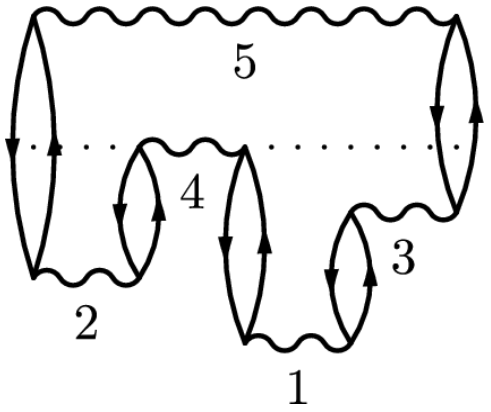


$$t_{ij}^{ab} = \ldots + \frac{\sum_{kc} V_{ic}^{ak} t_{kj}^{cb}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b + \mathrm{i}\eta} + \ldots$$

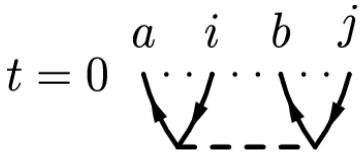


  - one more loop, one more hole, gives positive Fermion sign
  - more cases to come ...

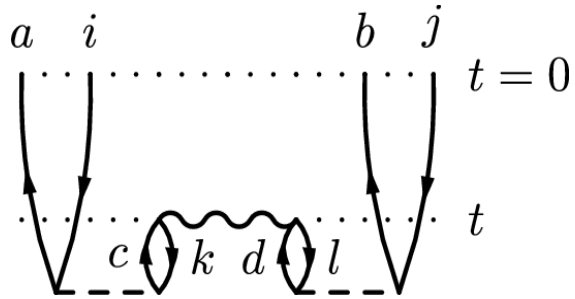
drCCD amplitudes (5)



- 4th case, found in interaction 4
  - two different particle/hole pairs merge to one
  - left pair created at interaction 2
    right pair created at interaction 1
  - merging occurs at any time t<0, dotted line
  - amplitudes needed twice: quadratic contribution

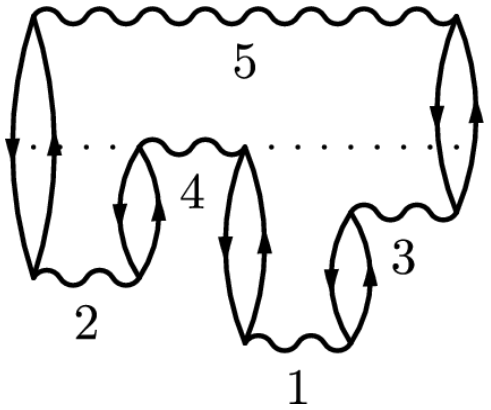


$$t_{ij}^{ab} = \ldots + \frac{\sum_{klcd} t_{ik}^{ac} V_{cd}^{kl} t_{lj}^{db}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b + \mathrm{i}\eta} \cdot$$



  - two more loops, two more holes give positive Fermion sign
  - last case

Random Phase Approximation from drCCD

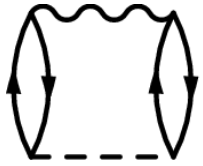


- 4 cases summed to drCCD amplitude equations
  - in insulators limit $\eta \to 0^+$ exists for all states

$$(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)\, t_{ij}^{ab} =$$

$$V_{ij}^{ab} + \sum_{kc} t_{ik}^{ac} V_{cj}^{kb} + \sum_{kc} V_{ic}^{ak} t_{kj}^{cb} + \sum_{klcd} t_{ik}^{ac} V_{cd}^{kl} t_{lj}^{db}$$

  - quadratic, can only be solved by iteration
  - using Shanks transform, 8 iterations sufficient for 6 digits precision
- last interaction, here interaction 5, closes the ring, giving RPA



$$= \frac{1}{2} \sum_{ijab} t_{ij}^{ab} V_{ab}^{ij}$$

  - two more loops, two more holes give positive Fermion sign
  - amplitudes have left/right symmetry → whole diagram symmetric

More about drCCD

- direct ring Coupled Cluster Doubles amplitudes subset of Coupled Cluster Singles Doubles amplitudes, excluding e.g.

- (canonical) CCSD: $O(N^6)$, (canonical) drCCD: $O(N^5)$
  - using decomposition of Coulomb matrix

$$V_{sr}^{pq} = \iint \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \psi_p^*(\mathbf{x})\psi_q^*(\mathbf{x}')\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, \psi_r(\mathbf{x}')\psi_s(\mathbf{x})$$

  - into

$$V_{sr}^{pq} = \int \frac{\mathrm{d}\mathbf{G}}{(2\pi)^3}\, \chi_s^p(\mathbf{G})\, \chi_q^{r*}(\mathbf{G}) \qquad \chi_q^p(\mathbf{G}) = \sqrt{\frac{4\pi}{\mathbf{G}^2}} \int \mathrm{d}\mathbf{x}\, \psi_p^*(\mathbf{x}) e^{\mathbf{i}\mathbf{r}\cdot\mathbf{G}} \psi_q(\mathbf{x})$$

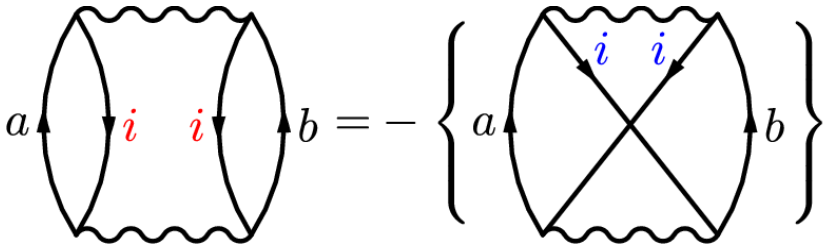
$$(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)\, t_{ij}^{ab} = \ldots + \sum_{ck} t_{ik}^{ac} V_{cj}^{kb} + \ldots$$

  - instead one $O(N^6)$ contraction
  - $\sigma_i^a(\mathbf{G}) = \sum_{ck} t_{ik}^{ac} \chi_c^k(\mathbf{G})$ tions

$$(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)\, t_{ij}^{ab} = \ldots + \int \frac{\mathrm{d}\mathbf{G}}{(2\pi)^3}\, \sigma_i^a(\mathbf{G}) \chi_b^{j*}(\mathbf{G}) + \ldots$$

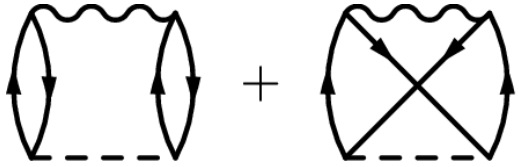
Exchange in drCCD

- violations of Pauli principle in rings would be corrected by exchange:



$$(-1)^{(2+2)}\,\frac{1}{2}\,\frac{V_{ii}^{ab}V_{ab}^{ii}}{\varepsilon_i+\varepsilon_i-\varepsilon_a-\varepsilon_b} = -\left\{(-1)^{(1+2)}\,\frac{1}{2}\,\frac{V_{ii}^{ab}V_{ab}^{ii}}{\varepsilon_i+\varepsilon_i-\varepsilon_a-\varepsilon_b}\right\}$$

- $O(N^5)$ time requires ring structure so no exchange while building amplitudes
- however, terminating amplitudes with exchange is for free



$$= \frac{1}{2}\sum_{ijab} t_{ij}^{ab}V_{ab}^{ij} - t_{ij}^{ab}V_{ab}^{ji}$$

  - one more loop, two more holes give negative Fermion sign
  - termed *second order screened exchange* (SOSEX)

Acknowledgement

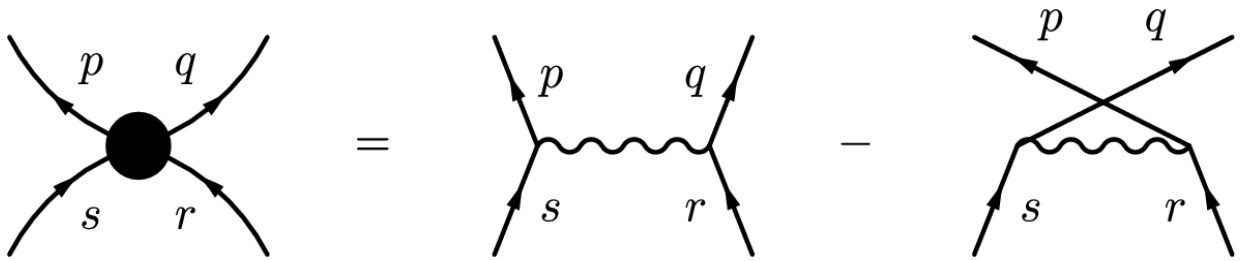
FWF for financial support

The group for their great work

You for listening

Hugenholtz diagrams

- anti-symmetry of wave function not contained in *single* Goldstone/Feynman diagram, only when taking *all*
- anti-symmetry can be intrinsically incorporated into any *single* diagram using



- called *Hugenholtz* diagrams
- however,
  - Fermion sign and
  - symmetry more difficult to assess