Section 9.1: The Coulomb Interaction and Perturbation Theory

What do we want to achieve?

The aim is to calculate material properties via Green's functions by treating the Coulomb interaction as a perturbation. Since the non-interacting problem can be solved exactly, the strategy is to expand around that solution.

Key Ideas and Equations

- **Analogy with Scattering Theory:** In scattering theory, an unperturbed state $|\phi_0\rangle$ is modified by a perturbation $\hat{V}$. The Lippmann–Schwinger equation reads

$$|\phi\rangle = |\phi_0\rangle + (\omega - \hat{H}_0)^{-1}\,\hat{V}\,|\phi\rangle, \tag{9.1}$$

  which can be reformulated using the non-interacting Green's function

$$G_0 \equiv (\omega + i\eta - \hat{H}_0)^{-1}, \quad \eta \to 0^+,$$

  so that

$$|\phi\rangle = (1 - G_0\,\hat{V})^{-1}|\phi_0\rangle. \tag{9.2}$$

- **Full Green's Function and Dyson Equation:** Define the full Green's function by

$$G \equiv (1 - G_0\,\hat{V})^{-1} G_0,$$

  which satisfies the Dyson equation:

$$G = G_0 + G_0\,\hat{V}\,G.$$

  Its perturbative expansion (the Born series) is

$$G = G_0 + G_0\,\hat{V}\,G_0 + G_0\,\hat{V}\,G_0\,\hat{V}\,G_0 + \cdots .$$

- **Application to Many-Body Systems:** For a full many-body Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, the full retarded Green's function is

$$G_{\mathrm{tot}}(\omega) = (\omega + i\eta - \hat{H})^{-1}.$$

  In strict analogy with the scattering case, one writes

$$G_{\mathrm{tot}}(\omega) = G^{(0)}_{\mathrm{tot}}(\omega) + G^{(0)}_{\mathrm{tot}}(\omega)\,\hat{V}\,G_{\mathrm{tot}}(\omega), \tag{9.3}$$

  with the expansion

$$G_{\mathrm{tot}}(\omega) = G^{(0)}_{\mathrm{tot}}(\omega) + G^{(0)}_{\mathrm{tot}}(\omega)\,\hat{V}\,G^{(0)}_{\mathrm{tot}}(\omega) + G^{(0)}_{\mathrm{tot}}(\omega)\,\hat{V}\,G^{(0)}_{\mathrm{tot}}(\omega)\,\hat{V}\,G^{(0)}_{\mathrm{tot}}(\omega) + \cdots . \tag{9.4}$$

  However, G_{tot} involves the interacting ground state, complicating direct evaluations.

- **Perturbation Theory for Energies and Wavefunctions:** Two common approaches are presented:

  (i) **Brillouin–Wigner Perturbation Theory:** The energy and wavefunction are expanded as

$$E = E_{ip} + \sum_{n=1}^{\infty} \langle \phi_{ip} | \, \hat{V} \left(\frac{1}{1-\hat{P}} \frac{1}{E - \hat{H}_0} \hat{V} \right)^{n-1} | \phi_{ip} \rangle, \tag{9.5}$$

  and

$$|\Phi\rangle = \sum_{n=0}^{\infty} \left(\frac{1}{1-\hat{P}} \frac{1}{E - \hat{H}_0} \hat{V} \right)^{n} | \phi_{ip} \rangle, \tag{9.6}$$

  where $\hat{P}$ projects onto the unperturbed state.

  (ii) **Rayleigh–Schrödinger Perturbation Theory:** In this approach the expansions become

$$E = E_{ip} + \sum_{n=1}^{\infty} \langle \phi_{ip} | \, \hat{V} \left(\frac{1}{E_{ip} - \hat{H}_0} (E_{ip} - E + \hat{V}) \right)^{n-1} | \phi_{ip} \rangle, \tag{9.7}$$

  and

$$|\Phi\rangle = \sum_{n=0}^{\infty} \left(\frac{1}{E_{ip} - \hat{H}_0} (E_{ip} - E + \hat{V}) \right)^{n} | \phi_{ip} \rangle. \tag{9.8}$$

  In both schemes the energy E appears self-consistently, and higher-order corrections become increasingly cumbersome.

- **Expansion Around a Mean-Field Hamiltonian (Møller–Plesset Perturbation Theory):** Instead of treating the full Coulomb interaction as the perturbation, one may include part of the interaction in a mean-field (e.g., Hartree–Fock) Hamiltonian:

$$\hat{H}_0 \to \hat{H}_0 + \text{Hartree–Fock mean field},$$

  and treat the remaining interaction $\hat{V}'$ perturbatively. In this approach:

  – The zeroth-order energy is the sum of occupied Hartree–Fock eigenvalues.

  – The first-order correction is given by

$$E^{(1)} = \langle \phi_{ip} | \, \hat{V} \, | \phi_{ip} \rangle = - \sum_{i<j} \left(v_{ijji} - v_{ijij} \right), \tag{9.9}$$

    so that $E_{ip} + E^{(1)}$ equals the Hartree–Fock total energy.

  – The second-order correction (MP2) is

$$E^{(2)} = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{empty}} \frac{|v_{ijab} - v_{ijba}|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \tag{9.11}$$

Although MP2 captures important correlation effects (e.g., van der Waals forces), higher orders (MP3, MP4, etc.) are computationally expensive and become less practical.

Section 9.2: Connecting the Interacting and Non-Interacting Systems

Objective

This section addresses the difficulty that the interacting ground state appears explicitly in the Green's function expressions. The strategy is to connect the non-interacting and interacting systems via *adiabatic switching*.

Key Ideas and Equations

- **Adiabatic Switching-On of the Interaction:** The Coulomb interaction is slowly switched on using a time-dependent form:

$$v_\eta(t) = v_c\, e^{-\eta|t|}, \quad \eta \to 0^+. \tag{1}$$

  At $t \to \pm\infty$ the interaction is off, while at $t = 0$ the full interaction is present.

- **Interaction Picture and Time Evolution:** In the interaction picture, states evolve with the interaction via

$$|\psi_I(t)\rangle = U_I(t, t_0)\, |\psi_I(t_0)\rangle,$$

  where the time-evolution operator is given by the Dyson series:

$$U_I(t, t_0) = T\left\{ \exp\left[-i \int_{t_0}^{t} V_I(t')\, dt' \right] \right\}. \tag{2}$$

  Here, the interaction-picture operator is

$$V_I(t) = e^{iH_0(t-t_0)}\, V\, e^{-iH_0(t-t_0)}.$$

- **Connecting Ground States:** By propagating the non-interacting ground state $|\phi_{ip}\rangle$ from $t = -\infty$ (or $+\infty$) using U_I, one defines states $|\phi_\eta^-(t)\rangle$ and $|\phi_\eta^+(t)\rangle$ that evolve into the interacting ground state. Expectation values are then obtained as

$$\langle O \rangle = \frac{\langle \phi_\eta^+ | O | \phi_\eta^- \rangle}{\langle \phi_\eta^+ | \phi_\eta^- \rangle}, \tag{3}$$

  ensuring that divergent phases from the adiabatic switching cancel.

- **Gell-Mann–Low Theorem:** This theorem guarantees that if the interaction is switched on adiabatically, the non-interacting ground state evolves into an eigenstate of the full Hamiltonian (ideally, the true interacting ground state). This allows one to express the interacting Green's function without an explicit reference to the complicated interacting wavefunction.
- **Interacting Green's Function:** The zero-temperature Green's function can then be written as

$$G(x,t;x',t') = -i\,\frac{\langle\phi_{ip}|\,T\{\psi_I(x,t)\psi_I^\dagger(x',t')\,S_\eta\}\,|\phi_{ip}\rangle}{\langle\phi_{ip}|\,S_\eta\,|\phi_{ip}\rangle}, \tag{4}$$

where

$$S_\eta \equiv U_I(\infty,-\infty)$$

is the full time-evolution (or scattering) operator in the interaction picture and T denotes time ordering.

Section 9.3: Telling the Story of Particles – Diagrams

The starting point is the formal expression for the interacting Green's function at zero temperature (see Eq. (9.22)):

$$G(x,t;x',t') = -i\,\frac{\langle\phi_{ip}|\,T\left[\psi(x,t)\psi^\dagger(x',t')\,\hat{S}\right]\,|\phi_{ip}\rangle}{\langle\phi_{ip}|\hat{S}|\phi_{ip}\rangle},$$

where the scattering (or time-evolution) operator is defined as

$$\hat{S}_\eta \equiv U_I(\infty,-\infty).$$

Using the interaction picture, the Coulomb interaction (treated as a perturbation) is given by (Eq. (9.23)):

$$\hat{V}_I(t) = \frac{1}{2}\int dx\,dx'\,\psi_I^\dagger(x,t)\,\psi_I^\dagger(x',t)\,v_c(r,r')\,\psi_I(x',t)\,\psi_I(x,t),$$

with the field operators in the interaction picture defined by

$$\psi_I(x,t) = e^{i\hat{H}_0(t-t_0)}\,\psi(x)\,e^{-i\hat{H}_0(t-t_0)}.$$

The expansion of the numerator in Eq. (9.22) can then be written as a series in powers of v_c. In compact notation (with $(x_1,t_1)\to 1$ etc.), one obtains (Eq. (9.24)):

$$-i\langle\phi_{ip}|\,T\left[\psi(x,t)\psi^\dagger(x',t')\,\hat{S}\right]\,|\phi_{ip}\rangle = G_0(x,t;x',t')$$
$$+\sum_{p=1}^{\infty}\left(\frac{i}{2}\right)^p\frac{1}{p!}\int\cdots\int d1\,d1'\cdots dp\,dp'\,v_c(1,1')\cdots v_c(p,p')\,G_0^{2p+1}(x,t,1,1',\ldots,p,p';\,x',t',1,1',\ldots,p,p').$$

Here, the one-body non-interacting Green's function is defined by (Eq. (9.25))

$$G_0(x,t;x',t') = \langle\phi_{ip}|\, T\left[\psi_I(x,t)\psi_I^\dagger(x',t')\right]|\phi_{ip}\rangle,$$

and the higher-order Green's functions (which describe the propagation of multiple particles) are defined by (Eq. (9.26))

$$G_0^{(s)}(1,2,\ldots,s;1',2',\ldots,s') = (-i)^s\langle\phi_{ip}|\, T\left[\psi_I(1)\psi_I(2)\cdots\psi_I(s)\,\psi_I^\dagger(s')\cdots\psi_I^\dagger(2')\psi_I^\dagger(1')\right]|\phi_{ip}\rangle.$$

For instance, the two-particle Green's function can be written as a determinant (Eq. (9.27)):

$$G_0^{(2)}(1,2;1',2') = G_0(1,1')\,G_0(2,2') - G_0(1,2')\,G_0(2,1') = \begin{vmatrix} G_0(1,1') & G_0(1,2') \\ G_0(2,1') & G_0(2,2') \end{vmatrix}.$$

Similarly, the three-particle Green's function $G_0^{(3)}$ can be expressed as a determinant (Eqs. (9.28) and (9.29)). Although tedious to derive from first principles, these determinant expressions show that the propagation of non-interacting fermions inherently obeys the antisymmetry principle.

Diagrammatic Representation

The idea is to translate these cumbersome multiple integrals into a graphical language:

- The zeroth-order contribution is simply a single propagator G_0 connecting the external points.
- At first order (with one Coulomb interaction insertion), the expansion (Eq. (9.24)) yields six terms [see Eq. (9.28)] which are represented by diagrams in Fig. 9.2. Here, the Coulomb interaction is drawn as a dashed line, and the propagators as solid lines with arrows.
- The diagrams are classified as *connected* (where the diagram cannot be separated into two without cutting a line) or *disconnected* (vacuum fluctuations). In the final expression for the Green's function, the disconnected diagrams cancel with corresponding contributions from the denominator (as ensured by the linked cluster theorem, discussed below).
- In higher orders (order p), one builds diagrams by connecting p Coulomb vertices with $2p+1$ Green's function lines. The final compact form for the interacting Green's function is given by (Eq. (9.36)):

$$G(c,c') = \sum_{p=0}^{\infty} i^p \int [d1\,d1'\cdots dp\,dp']\, v_c(1,1')\cdots v_c(p,p') \begin{vmatrix} G_0(c,c') & G_0(c,1) & \cdots & G_0(c,p') \\ G_0(1,c') & G_0(1,1^+) & \cdots & G_0(1,p') \\ \vdots & \vdots & \ddots & \vdots \\ G_0(p',c') & G_0(p',1) & \cdots & G_0(p',p'^+) \end{vmatrix}_{cd},$$

  where the subscript cd indicates that only *connected and topologically distinct* diagrams are retained.

1 Section 9.4: Making the Story Easier – Two Theorems

Two powerful theorems help simplify the combinatorially complex expansion of the Green's function.

1.1 Wick's Theorem

Wick's theorem provides a systematic way to express time-ordered products of field operators in terms of normal-ordered products plus all possible contractions. For two operators, the contraction is defined as (Eq. (9.30)):

$$\dot{A}\dot{B} = \hat{A}\hat{B} - N(\hat{A}\hat{B}),$$

and if the contraction yields a number (a c-number), then (Eq. (9.31)):

$$\dot{A}\dot{B} = \langle 0|\hat{A}\hat{B}|0\rangle.$$

For a product of many operators, Wick's theorem states that

$$\hat{A}\hat{B}\hat{C}\cdots\hat{X}\hat{Y}\hat{Z} = N(\hat{A}\hat{B}\hat{C}\cdots\hat{X}\hat{Y}\hat{Z}) + N\big(\dot{A}\dot{B}\hat{C}\cdots\hat{X}\hat{Y}\hat{Z}\big) + N\big(\dot{A}\hat{B}\dot{C}\cdots\hat{X}\hat{Y}\hat{Z}\big) + \cdots,$$

where all possible contractions (one pair, two pairs, etc.) are summed over (see Eq. (9.32)).

Using Wick's theorem, the higher-order non-interacting Green's functions can be expressed as determinants. For example, one obtains (Eq. (9.33)):

$$G_0^{(2n+1)}(c,1,1',2,2',\ldots,n,n';\, c',1,1',2,2',\ldots,n,n') = \sum_P (-1)^P\, G_0(c,\tilde{c}')\, G_0(1,\tilde{1})\cdots G_0(n',\tilde{n}'),$$

where the sum runs over all permutations P of the indices in the second set. This determinant structure naturally incorporates the antisymmetry required by fermions.

Linked Cluster Theorem

The linked cluster theorem guarantees that the disconnected (vacuum) diagrams cancel when one takes the ratio in Eq. (9.22). In other words, although the expansion contains many diagrams that represent vacuum fluctuations (disconnected pieces), they appear both in the numerator and the denominator. When these are properly normalized, only the *connected* diagrams remain. This is crucial because only connected diagrams contribute to observable quantities such as the interacting Green's function.

For example, if in the numerator a contribution factorizes into a connected part and a disconnected vacuum loop, the disconnected part is exactly canceled by a similar term in the denominator. As a result, the final expression for $G(c,c')$ (see Eq. (9.36)) involves only the topologically distinct, connected diagrams.

Application to the Calculation of the Green's Function

We now have everything in hand to write down the rules for constructing the perturbation series of the Green's function and to draw the corresponding Feynman diagrams. Recall that the zeroth-order contribution is simply the non-interacting one-body Green's function G_0. For each order p (i.e. with p Coulomb interaction insertions), the procedure is as follows:

Step 1: Construct Building Blocks:

- For each Coulomb interaction vertex (represented as a dashed line), add one Green's function line to each end.
- Since one Coulomb vertex is a two-body operator, it contributes two field operator pairs.
- Thus, for p vertices, we have p such building blocks.

Step 2: Assign Vertices:

- Each endpoint of an interaction line is a vertex; label it with a dot.
- A vertex represents a space–spin–time point $m = (r_m, \sigma_m, t_m)$.

Step 3: Combine the Building Blocks:

- Arrange the building blocks (each consisting of two Green's function lines and one interaction) so that every vertex is saturated by exactly two Green's function lines and the entire diagram is closed, except for one Green's function line that remains as a single leg.
- Also, add one extra G_0 to saturate the last vertex, thereby creating a second single leg.
- In this way, the resulting diagram has two external points c and c'.
- Note that a Green's function line that is closed on itself (representing the density) counts as two lines, and the direction of adjacent Green's function lines must be continuous.

Step 4: Draw Only Connected Diagrams:

- Retain only the connected, topologically distinct diagrams.
- With the rules above, a diagram at order p will always have $2p + 1$ propagator lines (i.e. $2p + 1$ occurrences of G_0).

Step 5: Translate Diagrams into Equations:

- Label each vertex by a space–spin–time point $m = (r_m, \sigma_m, t_m)$.
- An arrow from m' to m denotes the propagator $G_0(m, m')$.

- A dashed line represents the Coulomb interaction:

$$i\,v_c(m,m') = i\,v_c(r_m - r_{m'})\,\delta(t_{m'} - t_m).$$

- Integrate over all internal vertex coordinates.
- Each closed loop in the diagram contributes an extra factor of -1.

Step 6: Example at First Order:

- At first order ($p = 1$), two contributions arise (as illustrated in Fig. 9.2):
  - The first contribution represents a modification of the propagation due to the Hartree potential,

$$-i\,G_0\,v_c\,G_0\,G_0 = G_0 v_H G_0.$$

  - The second contribution is the corresponding exchange term, with the opposite sign.

Step 7: Higher Orders:

- For second order or higher, diagrams can involve combinations of several such scattering events.
- For instance, the two successive interactions shown on the left side of Fig. 9.4 illustrate one possibility.
- Additionally, a new type of diagram appears (as on the right side of Fig. 9.4) where an electron–hole pair (the bubble) is created, indicating that the propagating particle polarizes the system. This diagram plays a central role in later chapters (Chs. 10–15).

Step 8: Final Expression:

- All connected and topologically distinct diagrams contributing up to second order in the interaction are illustrated in Fig. 9.5.
- Table 9.1 summarizes the Feynman rules for converting these diagrams into equations.
- The final compact complete formula for the interacting Green's function is:

$$G(c,c') = \sum_{p=0}^{\infty} i^p \int \left[\prod_{j=1}^{p} v_c(j,j')\,d(j,j')\right] \det\Big[G_0\Big]_{cd}, \tag{9.36}$$

  where the determinant is taken over a matrix of $2p+1$ G_0 lines, and the subscript cd indicates that only connected diagrams are retained.

Example: Translating a $p = 2$ Diagram with Two Density Lines

Consider an order $p = 2$ contribution where the external one-body propagator is dressed by two interaction vertices. In this diagram, each Coulomb interaction vertex couples to a density line. Recall that a density line is represented by a Green's function with coinciding spatial (and nearly coinciding time) arguments, e.g.,

$$G_0(1, 1^+) \quad \text{which is proportional to the density } n(1).$$

Diagram Construction

According to the Feynman rules for constructing the perturbation series:

- **Building Blocks:** Each Coulomb interaction vertex is represented by a dashed line, with a Green's function line attached to each of its two endpoints (vertices).
- **For $p = 2$:**
  - Two interaction vertices are inserted.
  - Each vertex brings in two field operator pairs (or propagator lines).
  - In total, you have the external propagator (1 pair) plus $2 \times 2 = 4$ extra pairs, giving $1 + 4 = 5$ propagator lines.
- **Density Lines:** In our example, assume that at each vertex the attached propagator forms a closed loop (i.e. the two ends of the propagator coincide, representing the density). We denote these as $G_0(1, 1^+)$ at the first vertex and $G_0(2, 2^+)$ at the second vertex.

Translating the Diagram into an Equation

Let $c = (x, t)$ and $c' = (x', t')$ be the external coordinates. For a diagram where the external propagator is modified by two Hartree-like (density) insertions, the translation proceeds as follows:

1. Start with the external propagator $G_0(c, c')$.
2. Insert an interaction vertex at point 1. At this vertex, attach:
   - A propagator $G_0(c, 1)$ connecting the external point c to vertex 1.
   - A density loop $G_0(1, 1^+)$ representing the closed propagation (i.e. the density at point 1).
   - An interaction line $v_c(1, 1')$ connecting vertex 1 to itself (with the understanding that $1'$ is taken to be very near 1 so that $G_0(1, 1')$ becomes $G_0(1, 1^+)$).

3. Insert a second interaction vertex at point 2. At this vertex, attach:
   - A propagator $G_0(1,2)$ connecting vertex 1 to vertex 2.
   - A density loop $G_0(2,2^+)$ at vertex 2.
   - An interaction line $v_c(2,2')$ with $2'$ very close to 2.
4. Finally, connect vertex 2 to the external point c' via $G_0(2,c')$.

Thus, the contribution from this diagram is given by:

$$\Delta G(c,c') = i^2 \int d1\, d2\, G_0(c,1) \left[i\, v_c(1,1')\, G_0(1,1^+) \right] G_0(1,2) \left[i\, v_c(2,2')\, G_0(2,2^+) \right] G_0(2,c'),$$

where the integrals run over the internal coordinates (space, time, and spin) at points 1 and 2. Here, the factors $i\, v_c(1,1')$ and $i\, v_c(2,2')$ represent the Coulomb interactions at vertices 1 and 2, respectively, with the understanding that $1' \to 1^+$ and $2' \to 2^+$ to form the density loops.

Notes:

- The overall factor i^2 comes from having two interaction vertices.
- The product $G_0(1,1^+)$ is interpreted as the density $n(1)$, and similarly for $G_0(2,2^+)$.
- The final diagram has $2p+1 = 5$ Green's function lines, as expected for $p = 2$.
- In a complete expansion, one must sum over all topologically distinct, connected diagrams at this order. This is just one example.

Dyson Equation for the One-Particle Green's Function and the Self-Energy

We are now ready to cast our results in a form similar to Eqs. (9.3) and (9.4), but for the one-body Green's function. Starting from first order, each diagram has an ingoing and an outgoing non-interacting Green's function line. Therefore, as depicted schematically in Fig. 9.6, the final expression for the interacting Green's function can be written as the matrix equation

$$G = G_0 + G_0\, \Sigma_{\text{red}}\, G_0, \tag{9.37}$$

where we do not show the matrix indices. Here, Σ_{red} is the *reducible* (or improper) self-energy.

Reducible Self-Energy: By definition, Σ_{red} is the sum of all Feynman diagrams with no external lines. It is called *reducible* because it contains lower-order patterns that are simply linked by one Green's function line.

For example, one can cut the first diagram in Fig. 9.4 in the middle and be left with two identical first-order diagrams.

We now introduce the *proper* (or irreducible) self-energy, Σ, as defined in Sec. 7.2. This quantity is the sum of only those self-energy diagrams that cannot be separated into pieces by cutting a single Green's function line. Conversely, the improper self-energy is obtained by concatenating the proper contributions via G_0-lines. This relation is expressed as

$$\Sigma_{\text{red}} = \Sigma + \Sigma\, G_0\, \Sigma + \Sigma\, G_0\, \Sigma\, G_0\, \Sigma + \cdots = \Sigma + \Sigma\, G_0\, \Sigma_{\text{red}}. \tag{9.38}$$

Combining Eqs. (9.37) and (9.38) yields the Dyson equation (see also Eq. (7.10)):

$$G = G_0 + G_0\, \Sigma[G_0]\, G. \tag{9.39}$$

This equation is graphically represented in Fig. 9.7. Note that at this point the self-energy is given as a functional of G_0. Although the numerical result of the diagrammatic series depends on the system (through G_0 and v_c), the functional form is universal. In Chapter 8 the self-energy is instead presented as a functional of the fully interacting G; we discuss that further in Sec. 9.8.

Diagrammatic Interpretation: The diagrammatic representation illustrates how a low-order approximation to the proper self-energy generates contributions to G at all orders. For example, Fig. 9.8 shows the first-order contributions to the proper self-energy. These contributions are the Hartree potential (on the left) and the Fock exchange (on the right), both evaluated with the non-interacting G_0. When these self-energy contributions are inserted into the Dyson equation, the resulting interacting Green's function contains an infinite number of interaction lines, capturing the full effect of the Coulomb interaction.

Appendix I: Time Evolution in the Interaction Picture

We start by splitting the full Hamiltonian into a free part and an interaction part:

$$H = H_0 + V,$$

where H_0 is the non-interacting (free) Hamiltonian and V is the interaction term.

Operator Evolution

In the interaction picture, an operator O (denoted as O_S in the Schrödinger picture) is transformed according to:

$$O_I(t) = e^{iH_0(t-t_0)}\, O_S\, e^{-iH_0(t-t_0)}.$$

This means that the operator evolves under the free Hamiltonian H_0 only. Any explicit time dependence present in O_S is carried through.

State Evolution

In contrast to operators, the state vectors in the interaction picture evolve under the interaction V. The state $|\psi_I(t)\rangle$ is given by:

$$|\psi_I(t)\rangle = U_I(t, t_0)\, |\psi_I(t_0)\rangle,$$

where the time-evolution operator $U_I(t, t_0)$ obeys the differential equation:

$$\frac{d}{dt} U_I(t, t_0) = -i\, V_I(t)\, U_I(t, t_0),$$

with the initial condition:

$$U_I(t_0, t_0) = I.$$

Interaction Picture of the Interaction

The interaction V is expressed in the interaction picture by:

$$V_I(t) = e^{iH_0(t-t_0)}\, V\, e^{-iH_0(t-t_0)}.$$

Formal Solution: The Dyson Series

The formal solution for $U_I(t, t_0)$ is given by the Dyson series:

$$U_I(t, t_0) = T\left\{ \exp\left[-i \int_{t_0}^{t} V_I(t')\, dt' \right] \right\},$$

where T denotes the time-ordering operator. Time ordering is necessary because the interaction $V_I(t')$ at different times may not commute.

Summary

In summary:

- **Operator Evolution:** In the interaction picture, operators evolve with the free Hamiltonian:

$$O_I(t) = e^{iH_0(t-t_0)}\, O_S\, e^{-iH_0(t-t_0)}.$$

- **State Evolution:** The states evolve under the interaction through the time-evolution operator:

$$|\psi_I(t)\rangle = U_I(t,t_0)\,|\psi_I(t_0)\rangle,$$

  where

$$U_I(t,t_0) = T\left\{\exp\left[-i\int_{t_0}^{t} V_I(t')\,dt'\right]\right\}.$$

This separation of the evolution into a free part (handled by the operators) and an interaction part (handled by the states) is especially useful for developing perturbation theory, where V is treated as a small perturbation.

Appendix II: Crash Course on Feynman Diagrams in Many-Body Theory

Feynman diagrams provide a powerful graphical method to organize and compute the perturbative expansion in many-body quantum theory. In this appendix we present a crash course on Feynman diagrams in the context of many-body theory and discuss related topics such as the role of single and double excitations, Brillouin's theorem, and the treatment of vacuum fluctuations.

Basic Ingredients

Propagators (Green's Functions)

The **bare propagator** G_0 represents the amplitude for a particle to propagate from one space-time point to another in the absence of interactions. For example, in frequency space:

$$G_0(\omega) = \frac{1}{\omega + i\eta - \varepsilon_k},$$

where ε_k is the single-particle energy and η is an infinitesimal ensuring causality. In diagrams, G_0 is depicted as a solid line with an arrow indicating the direction of propagation.

Interaction Vertices

The Coulomb interaction (often the **bare Coulomb interaction**) is given by:

$$v_c(r - r') = \frac{e^2}{|r - r'|}.$$

In diagrams, it is represented by a dashed line connecting two vertices. Each vertex represents a space-time point at which the interaction occurs and is accompanied by an integration over that coordinate.

Feynman Rules

To translate a Feynman diagram into a mathematical expression, one generally follows these rules:

(a) **Assign Propagators:** For every solid line connecting two points x and x', include a factor $G_0(x, x')$ (or the dressed propagator G if self-energy insertions are resummed).

(b) **Vertices:** Each interaction vertex contributes an integration over the corresponding space-time coordinate and a factor of the interaction v_c. Conservation of energy and momentum is imposed at each vertex (typically via delta functions).

(c) **Symmetry Factors and Signs:** For fermions, account for the minus signs arising from anticommutation relations and include symmetry factors to prevent overcounting.

(d) **Time Ordering:** The overall expression is time-ordered. This is handled by the time-ordering operator T in the Dyson series:

$$U_I(t, t_0) = T\left\{ \exp\left[-i \int_{t_0}^{t} V_I(t')\, dt' \right] \right\}.$$

Diagrammatic Expansion of the Green's Function

The full interacting one-particle Green's function G can be expanded in powers of the interaction:

$$G = G_0 + G_0\, \hat{V}\, G_0 + G_0\, \hat{V}\, G_0\, \hat{V}\, G_0 + \cdots .$$

In diagrammatic language:

- **Zeroth Order:** A single G_0 line between the external points.
- **First Order:** Diagrams with one interaction vertex, such as the Hartree (direct) and Fock (exchange) diagrams. Notably, in a Hartree–Fock reference the contribution from single excitations vanishes (see Brillouin's theorem below).
- **Second Order and Higher:** Diagrams with two or more vertices include processes such as electron–hole pair excitations (bubble diagrams) that capture polarization and screening.

Single and Double Excitations and Their Diagrammatic Order

Single Excitations

A single excitation involves promoting one electron from an occupied orbital to a virtual (unoccupied) orbital, thereby creating an electron–hole pair. However, in the context of a Hartree–Fock ground state:

- Brillouin's theorem ensures that the matrix element between the Hartree–Fock state $|\Phi_{\mathrm{HF}}\rangle$ and any singly excited determinant $|\Phi_i^a\rangle$ is zero:

$$\langle \Phi_{\mathrm{HF}} | \hat{H} | \Phi_i^a \rangle = 0.$$

- Thus, the first-order correction due to single excitations vanishes.

Double Excitations

Double excitations involve the simultaneous excitation of two electrons (i.e., two electron–hole pairs). Since the Coulomb interaction is a two-body operator:

- Double excitations occur at second order in perturbation theory, involving two vertices.
- These contributions do not vanish due to Brillouin's theorem and are crucial for capturing electron correlation, screening, and van der Waals interactions.

Brillouin's Theorem

Brillouin's theorem is a key result in Hartree–Fock theory. It states that if $|\Phi_{\mathrm{HF}}\rangle$ is the Hartree–Fock ground state and $|\Phi_i^a\rangle$ is a singly excited determinant (an electron is excited from occupied orbital i to unoccupied orbital a), then:

$$\langle \Phi_{\mathrm{HF}} | \hat{H} | \Phi_i^a \rangle = 0.$$

Implications

- The Hartree–Fock ground state is variationally optimized such that first-order mixing with singly excited determinants is zero.
- Therefore, the contribution of single excitations in first-order perturbation theory vanishes, and observable electron correlation effects must arise from double (or higher) excitations.

Appendix III: The Slater–Condon Rules

The Slater–Condon rules provide a systematic procedure for evaluating matrix elements of one-body and two-body operators between Slater determinants. Since Slater determinants are antisymmetrized products of single-particle orbitals, these rules greatly simplify the computation of expectation values and transition matrix elements in many-electron systems. They form the basis for methods such as Hartree–Fock theory, configuration interaction, and many-body perturbation theory.

1.2 One-Body Operators

Consider a one-body operator $\hat{O}^{(1)}$ (e.g., the kinetic energy or an external potential), which acts on single-particle states. Let $|\Phi\rangle$ denote a Slater determinant built from a set of orbitals.

- **Diagonal matrix elements:** When the bra and ket are the same Slater determinant,

$$\langle\Phi|\hat{O}^{(1)}|\Phi\rangle = \sum_{i\in\text{occ}} \langle\phi_i|\hat{o}^{(1)}|\phi_i\rangle,$$

  where the sum runs over all occupied orbitals.

- **Off-diagonal matrix elements:** If $|\Phi_i^a\rangle$ is a determinant that differs from $|\Phi\rangle$ by replacing an occupied orbital ϕ_i with a virtual orbital ϕ_a, then

$$\langle\Phi_i^a|\hat{O}^{(1)}|\Phi\rangle = \langle\phi_a|\hat{o}^{(1)}|\phi_i\rangle.$$

  For determinants differing by more than one orbital, the matrix element is zero.

1.3 Two-Body Operators

Next, consider a two-body operator $\hat{O}^{(2)}$, such as the electron–electron Coulomb interaction. Its matrix elements between Slater determinants are more complex, but the Slater–Condon rules dictate that:

- **Diagonal matrix elements:** For a determinant $|\Phi\rangle$,

$$\langle\Phi|\hat{O}^{(2)}|\Phi\rangle = \frac{1}{2}\sum_{i,j\in\text{occ}} \Big(\langle\phi_i\phi_j|\hat{o}^{(2)}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{o}^{(2)}|\phi_j\phi_i\rangle\Big).$$

- **Off-diagonal matrix elements:** If $|\Phi_{ij}^{ab}\rangle$ is a determinant obtained from $|\Phi\rangle$ by replacing orbitals ϕ_i and ϕ_j with orbitals ϕ_a and ϕ_b, then the nonzero matrix element is given by

$$\langle\Phi_{ij}^{ab}|\hat{O}^{(2)}|\Phi\rangle = \langle\phi_a\phi_b|\hat{o}^{(2)}|\phi_i\phi_j\rangle - \langle\phi_a\phi_b|\hat{o}^{(2)}|\phi_j\phi_i\rangle.$$

If the determinants differ by more than two orbitals, the matrix element vanishes.