UNIVERSITY OF OSLO

FYS4480 Oral Exam

Quantum mechanics for many-particle systems

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Introduction

Contents

Notation

Here, we follow the notation of having states $ijk\ldots$ refer to occupied states, and $abc\ldots$ refer to unoccupied states, typically below and above the Fermi level, respectively. From a reference state $|\Phi_0\rangle$ with N particles, we write a 1-particle-1-hole ($1p$–$1h$) excitation as

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle, \tag{1}$$

and similarly for $2p$–$2h$, $3p$–$3h$, etc.
We write a state Φ as a Slater determinant

$$\Phi(x_1, x_2, \ldots, x_N, \alpha, \beta, \ldots, \gamma) = \begin{bmatrix} \psi_\alpha(x_1) & \psi_\beta(x_1) & \cdots & \psi_\gamma(x_1) \\ \psi_\alpha(x_2) & \psi_\beta(x_2) & \cdots & \psi_\gamma(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_\alpha(x_N) & \psi_\beta(x_N) & \cdots & \psi_\gamma(x_N) \end{bmatrix} \tag{2}$$

for a set of single-particle functions $\{\psi_\alpha\}$.

Motivation

We are, in essence, interested in finding the ground state energy of a many-body system, that is, solving the eigenvalue problem

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle, \tag{3}$$

where $\hat{H}$ is the Hamiltonian operator and $|\Psi_0\rangle$ is the ground state wave function, such that the ground state energy E_0 is minimized.

The complexity arises from the fact that the exact solution cannot typically be found for systems with more than a few particles, and we must resort to approximations.

Full configuration interaction

Contents

Full configuration interaction theory

In full configuration interaction (FCI) theory, we seek to write the wave function as a linear combination of all possible Slater determinants, that is, all possible configurations of the system, truncated at some level.

That is, we wish to write the wave function as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ia} C_i^a|\Phi_i^a\rangle + \sum_{ijab} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots, \tag{4}$$

where the coefficients C are determined by solving the eigenvalue problem.

Slater determinants for pairing model

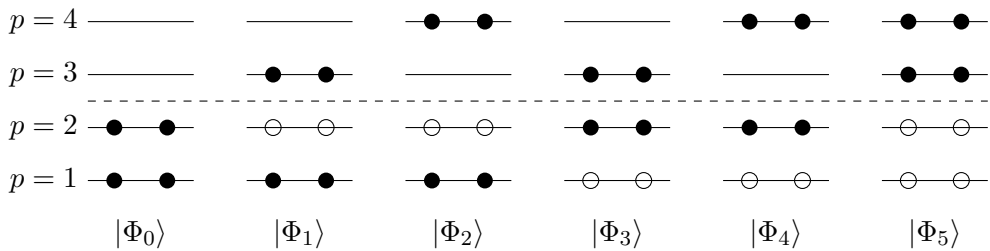


Figure: Schematic representation of the six possible Slater determinants for a system with four particles, under the constraint of no broken pairs, total spin $S = 0$, considering only the four lowest levels $p = 1, 2, 3, 4$.

Solving the problem

In solving the system, one first has to set up the Hamiltonian matrix, with elements

$$H_{i,j} = \langle \Phi_i | \hat{H} | \Phi_j \rangle, \tag{5}$$

and then diagonalize the matrix to find the eigenvalues and eigenvectors. The ground state energy can then be found as the lowest eigenvalue, with the corresponding eigenvector giving the coefficients C.

FCI is exact, but computationally expensive, as the number of configurations grows factorially with the number of energy levels included. Approximative methods are therefore required.

Hartree-Fock

Contents

Hartree-Fock theory

In Hatree-Fock (HF) theory, we assume that the system can be approximated by a single Slater determinant Φ, and we seek to find the wavefunctions $|\psi_\alpha\rangle$ that minimize the energy

$$E_0 = \left\langle \Phi | \hat{H} | \Phi \right\rangle. \tag{6}$$

This gives rise to the HF equations

$$\hat{h}^{\mathrm{HF}} |\psi_\alpha\rangle = \varepsilon_\alpha |\psi_\alpha\rangle, \tag{7}$$

where $\hat{h}^{\mathrm{HF}} = \hat{t} + \hat{u}_{\mathrm{ext}} + \hat{u}^{\mathrm{HF}}$, called the Fock operator, is an effective one-body operator. Here, $\hat{u}^{\mathrm{HF}}$ is the mean potential from the other particles, of the form

$$\langle p | \hat{u}^{\mathrm{HF}} | q \rangle = \sum_i \langle pi | V | qi \rangle_{AS}. \tag{8}$$

Varying the wave functions

As Eq. (8) depends on the eigenfunctions, Eq. (7) is nonlinear. We therefore solve it iteratively, until convergence is reached[1]. Varying the wave functions directly lead to a set of coupled integro-differential equations, wherein the integrals need to be computed at each iteration.

Another, more computationally efficient approach, is to expand the wave functions in a basis of known functions, and vary the coefficients of the expansion. We do this by a unitary transformation to a new basis p,

$$\psi_p = \sum_\alpha C_{p\alpha}\phi_\alpha, \tag{9}$$

where we now vary the coefficients $C_{p\alpha}$.

[1] If it converges at all.

The HF equations

Varying the coefficients, we find

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{p\gamma} = \varepsilon^{\mathrm{HF}}_{p} C_{p\alpha}, \tag{10}$$

where

$$h^{\mathrm{HF}}_{\alpha\gamma} = \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\beta\delta} \rho_{\beta\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \tag{11}$$

Here, $\rho_{\beta\delta}$ is the density matrix, defined as $\rho_{\beta\delta} = \sum_i \langle \beta | i \rangle \langle i | \delta \rangle = \sum_i C_{i\beta} C^*_{i\delta}$. Eq. (10) is in effect nothing more than an eigenvalue problem, and the HF equations are solved by diagonalizing the matrix h^{HF} repeatedly. The efficiency comes from the fact that the integrals in Eq. (11) need only be computed once, and the density matrix is updated at each iteration from the eigenvectors.

Many-body pertubation theory

Contents

Many-body pertubation theory

In many-body pertubation theory (MBPT), we seek to find the ground state energy by expanding the wave function in a series of pertubations to the Hamiltonian. We assume that the exact solution can be written as

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m |\Phi_m\rangle, \tag{12}$$

and that the ground state is dominated by the reference state

$$\hat{H}_0|\Phi_0\rangle = W_0|\Phi_0\rangle. \tag{13}$$

Correlation energy

The Schrödinger equation is then

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle, \tag{14}$$

which gives

$$\left\langle \Phi_0|\hat{H}|\Psi_0 \right\rangle = E. \tag{15}$$

Combining this with

$$\left\langle \Psi_0|\hat{H}_0|\Phi_0 \right\rangle = W_0, \tag{16}$$

and using the fact that $\hat{H}, \hat{H}_0$ are Hermitian, we find

$$\left\langle \Phi_0|\hat{H}_I|\Psi_0 \right\rangle = E - W_0 = \Delta E, \tag{17}$$

where ΔE is the correlation energy.

Perturbed expression

Introducing the energy variable ω, we can derive

$$\Delta E = \sum_{i=0}^{\infty} \left\langle \Phi_0 \middle| \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E + \hat{H}_I \right) \right\}^i \middle| \Phi_0 \right\rangle. \tag{18}$$

This is in reality nothing more than a rewrite of Eq. (17), but serves as a starting point for the pertubation expansion. It contains the unknown energy E, as well as the variable ω, and hence we need further assumptions to solve it.

Brillouin-Wigner pertubation theory

In Brillouin-Wigner pertubation theory (BWPT), we set $\omega = E$ in Eq. (18), and we find

$$\begin{aligned}\Delta E &= \sum_{i=0}^{\infty} \left\langle \Phi_0 \right| \hat{H}_I \left\{ \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \right\}^i \left| \Phi_0 \right\rangle \\ &= \left\langle \Phi_0 \right| \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \dots \right) \left| \Phi_0 \right\rangle .\end{aligned} \tag{19}$$

The equations then become rather simple, as compared with Eq. (18), with the exception on the unknown energy E. It can however be solved iteratively, for an initial guess of E.

Rayleigh-Schrödinger pertubation theory

In Rayleigh-Schrödinger pertubation theory (RSPT), we set $\omega = W_0$ in Eq. (18), and we find

$$\begin{aligned}\Delta E &= \sum_{i=0}^{\infty} \Big\langle \Phi_0 \big| \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} \Big(W_0 - E + \hat{H}_I \Big) \right\}^i \big| \Phi_0 \Big\rangle \\ &= \sum_{i=0}^{\infty} \Big\langle \Phi_0 \big| \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} \Big(\hat{H}_I - \Delta E \Big) \right\}^i \big| \Phi_0 \Big\rangle .\end{aligned} \tag{20}$$

As $\hat{Q}\Delta E|\Phi_0\rangle = 0$, we can write

$$\Delta E = \Big\langle \Phi_0 \big| \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \Big(\hat{H}_I - \Delta E \Big) \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \ldots \big| \Phi_0 \Big\rangle . \tag{21}$$

Order by order contributions

Eq. (21) allows us to define the recursive formula

$$\Delta E = \sum_{i=1}^{\infty} \Delta E^{(i)}, \tag{22}$$

where the first few terms are, writing $\langle \hat{A} \rangle = \langle \Phi_0 | \hat{A} | \Phi_0 \rangle$,

$$\Delta E^{(1)} = \left\langle \hat{H}_I \right\rangle \tag{23}$$

$$\Delta E^{(2)} = \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle \tag{24}$$

$$\Delta E^{(3)} = \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle - \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \left\langle \hat{H}_I \right\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle. \tag{25}$$

Order by order contributions

With the previous formula, we can find the correlation energy up to a given order of contributions. This method is however not without its drawbacks. For one, there is no guarantee that the series will converge, and the method is not variational. This entails that we will not necessarily get an improved estimate from including more terms in the series.

Coupled-Cluster theory

Contents

Coupled-Cluster theory

In coupled-cluster (CC) theory, we seek to write the wave function as

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle, \tag{26}$$

where $\hat{T}$ is the cluster operator, defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots, \tag{27}$$

with $\hat{T}_n$ being the n-body cluster operator. The first two such operators are

$$\hat{T}_1 = \frac{1}{(1!)^2}\sum_{ai} t_i^a a_a^\dagger a_i, \quad \text{and} \quad \hat{T}_2 = \frac{1}{(2!)^2}\sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \tag{28}$$

With this, we also define the similarity transformed Hamiltonian $\overline{H_N} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$.

Determining the cluster amplitudes

We determine the cluster amplitudes $t_{i_1 \dots i_n}^{a_1 \dots a_n}$ by solving the equations

$$\left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \overline{H_N} | \Phi_0 \right\rangle = 0, \tag{29}$$

which is derived from the equations

$$\left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \hat{H} e^{\hat{T}} | \Phi_0 \right\rangle = E_0 \left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | e^{\hat{T}} | \Phi_0 \right\rangle. \tag{30}$$

If we were to solve this exactly without truncations, i.e. by including up to np–nh excitations, we would have the same complexity as FCI. We therefore need to truncate the series, and the most common truncation is at CCSD, where we include up to $2p$–$2h$ excitations.

Truncated Couple-Cluster

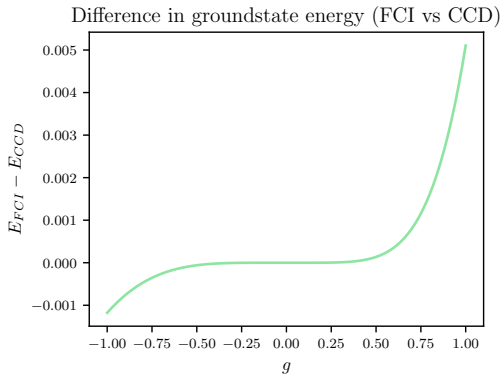
In order to make the method computationally feasible, we truncate the series at some level. By doing this, the method is non-variational.

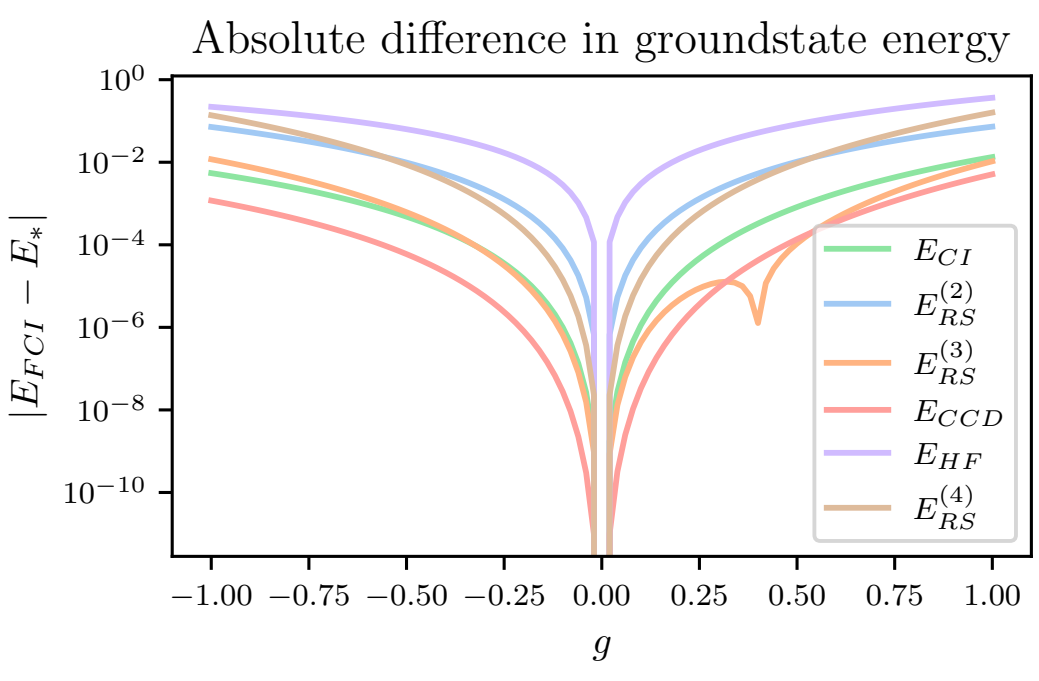
We solve the equations iteratively, and in this case we need an initial guess for the cluster amplitudes. A common choice in CCD is then to use the first order wave operator from MPBT, setting

$$(t_{ij}^{ab})^{(0)} = \frac{\langle ab|V|ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \tag{31}$$

CCD results for the pairing model

Returning to the pairing model, we have the ground state energy difference for the CCD method, as a function of the interaction strength g.




Absolute difference in groundstate energy
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
$|E_{FCI} - E_*|$
−1.00 −0.75 −0.50 −0.25 0.00 0.25 0.50 0.75 1.00
g
E_{CI}
$E_{RS}^{(2)}$
$E_{RS}^{(3)}$
E_{CCD}
E_{HF}
$E_{RS}^{(4)}$

Derivation of the HF equations

Contents

Derivation of the HF equations

In the original basis α we have the energy functional

$$E[\Phi] = \left\langle \Phi|\hat{H}|\Phi \right\rangle = \sum_{\alpha}\langle\alpha|\hat{h}_0|\alpha\rangle + \frac{1}{2}\sum_{\alpha\beta}\langle\alpha\beta|V|\alpha\beta\rangle_{AS}. \tag{32}$$

By way of varying the coefficients, the HF equations are found by introducing the new basis p defined by the unitary transformation

$$\psi_p = \sum_{\alpha} C_{p\alpha}\phi_{\alpha}, \tag{33}$$

and minimizing the energy functional

$$E[\Phi^{\mathrm{HF}}] = \left\langle \Phi^{\mathrm{HF}}|\hat{H}|\Phi^{\mathrm{HF}} \right\rangle = \sum_{i}\langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle_{AS} \tag{34}$$

with respect to the coefficients $C_{p\alpha}$.

Introducing Lagrange multipliers

Defining the functional in Eq. (34) as a functional of the coefficients $C_{p\alpha}$, we have

$$E_0[C] = \sum_i \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C^*_{i\alpha} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \tag{35}$$

As we have orthonormal basis functions, we have

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{36}$$

so we introduce the functional

$$F[C] = E_0[C] - \sum_i \lambda_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{37}$$

where λ_i are the Lagrange multipliers enforcing orthonormality.

Minimizing F

Minimizing F with respect to $C^*_{i\alpha}$, we wish to solve

$$\frac{\mathrm{d}F}{\mathrm{d}C^*_{i\alpha}}[C] = \frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\left[E_0[C] - \sum_j \lambda_j \sum_\alpha C^*_{j\alpha}C_{j\alpha}\right] = 0. \tag{38}$$

Term by term we have

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\sum_i\sum_{\alpha\beta} C^*_{i\alpha}C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle \tag{39}$$

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta} C^*_{i\alpha}C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}, \tag{40}$$

Minimizing F, cont.

and finally

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}} \sum_i \lambda_i \sum_\alpha C^*_{i\alpha} C_{i\alpha} = \lambda_i C_{i\alpha}. \tag{41}$$

Combining these terms, we have

$$\sum_\beta C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_j \sum_{\beta\gamma\delta} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} - \lambda_i C_{i\alpha} = 0. \tag{42}$$

Recognizing λ_i as the eigenvalues $\varepsilon_i^{\mathrm{HF}}$, we can write this as

$$\sum_\gamma \left[\langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_j \sum_{\beta\delta} C^*_{j\beta} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} \right] C_{p\gamma} = \varepsilon_p^{\mathrm{HF}} C_{p\alpha}. \tag{43}$$

Hartree-Fock equations found

This finally results in the HF equations

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{p\gamma} = \varepsilon^{\mathrm{HF}}_{p} C_{p\alpha}. \tag{44}$$

Derivation of MBPT

Contents

Derivation of many-body pertubation expansion

We have

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle \tag{45}$$

$$\left(\hat{H}_0 + \hat{H}_I\right)|\Psi_0\rangle = E|\Psi_0\rangle \tag{46}$$

$$-\hat{H}_0|\Psi_0\rangle = \left(-E + \hat{H}_I\right)|\Psi_0\rangle \tag{47}$$

$$\left(\omega - \hat{H}_0\right)|\Psi_0\rangle = \left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle, \tag{48}$$

where ω is an energy variable dependent on the expansion method. Assuming the resolvent of $\left(\omega - \hat{H}_0\right)$ exists, we can then rewrite the Schrödinger equation as

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle. \tag{49}$$

Combining with projection operators

With the projection operators

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0| \quad \text{and} \quad \hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|, \tag{50}$$

we can then write

$$\begin{aligned} |\Psi_0\rangle &= \left(\hat{P} + \hat{Q}\right)|\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle \\ &= |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle. \end{aligned} \tag{51}$$

Solving this in an iterative fashion, with an initial guess for $|\Psi_0\rangle = |\Phi_0\rangle$, we have

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right) \right\}^i |\Phi_0\rangle. \tag{52}$$