TCC Electronic Structure Module
L4: Møller–Plesset Perturbation Theory

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Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

L1 Exact and inexact wavefunctions

L2 Hartree–Fock theory

L3 Configuration Interaction theory

L4 Møller–Plesset perturbation theory

L5 Coupled-cluster theory

L6 Properties and excited states

L7 Density Functional Theory

L8 Density Functional Approximations

Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

1 Introduction

Configuration interaction theory is straightforward to apply, but it is linear theory. The only way to account for high-order correlation effects is to directly include configurations with high-order excitations and due to the combinatoric increase in the dimension of the Hamiltonian matrix, the calculation quickly becomes impractical. An alternative approach to electron correlation is provided by perturbation theory. Here, instead of variationally minimising the parameters in a wavefunction expansion, the inter-particle interactions missing in Hartree–Fock theory are considered as a perturbation to the Hartree–Fock state and energy corrections due to the interactions are computed by considering the response of the wavefunction to the perturbation.

2 General non-degenerate perturbation theory

You have covered this material in earlier lectures, so only a very brief summary is provided here.

In quantum mechanical perturbation theory we select a reference Hamiltonian $\hat{H}_0$ for which we know the eigenstates and that is as close as possible to the true Hamiltonian $\hat{H}$. The perturbation is then $\hat{H}_1 = \hat{H} - \hat{H}_0$. We define a strength parameter λ for the perturbation, where $\lambda = 0$ is the unperturbed system and $\lambda = 1$ is the true Hamiltonian. If the perturbation $\hat{H}_1$ is sufficiently weak, the wavefunction and energy can be expanded as a power series in λ

$$(\hat{H}_0 + \lambda\hat{H}_1)(\Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \cdots) = (E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots)(\Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \cdots) \tag{1}$$

We are free to select a normalisation convention and it is convenient to chose intermediate normalisation where $\langle\Psi_0|\Psi_0\rangle = 1$ and $\langle\Psi|\Psi_0\rangle = 1$, which results in $\langle\Psi_n|\Psi_0\rangle = 0\ \forall\ n \neq 0$. Equating powers of λ gives

$$\begin{aligned}
\hat{H}_0\Psi_0 &= E_0\Psi_0 && (2)\\
(\hat{H}_0 - E_0)\Psi_1 &= (E_1 - H_1)\Psi_0 && (3)\\
(\hat{H}_0 - E_0)\Psi_2 &= (E_1 - H_1)\Psi_1 + E_2\Psi_0 && (4)\\
&\vdots
\end{aligned}$$

The first equation is satisfied because of our choice that we know the eigenstates of $\hat{H}_0$. The second equation can be used to obtain both E_1 and Ψ_1. Projecting on the left by $\langle\Psi_0|$ and integrating gives and equation for E_1

$$\begin{aligned}
\langle\Psi_0|(\hat{H}_0 - E_0)|\Psi_1\rangle &= \langle\Psi_0|(\hat{H}_1 - E_1)|\Psi_0\rangle && (5)\\
0 &= \langle\Psi_0|\hat{H}_1|\Psi_0\rangle - E_1 && (6)
\end{aligned}$$

At first order in the perturbation, the energy correction is the expectation value of the perturbation using the unperturbed wavefunction. Projecting on the left by $\langle\Psi_1|$ and integrating gives and equation for Ψ_1

$$\begin{aligned}
\langle\Psi_1|(\hat{H}_0 - E_0)|\Psi_1\rangle &= \langle\Psi_1|(\hat{H}_1 - E_1)|\Psi_0\rangle && (7)\\
\langle\Psi_1|(\hat{H}_0 - E_0)|\Psi_1\rangle &= \langle\Psi_1|\hat{H}_1|\Psi_0\rangle && (8)
\end{aligned}$$

Ψ_1 is the intial, or first-order response of the wavefunction to the perturbation. Projecting the third equation on the left by $\langle\Psi_0|$ and integrating gives

$$\langle\Psi_0|(\hat{H}_0 - E_0)|\Psi_2\rangle = \langle\Psi_0|(\hat{H}_1 - E_1)|\Psi_1\rangle + \langle\Psi_0|E_2|\Psi\rangle \tag{9}$$

$$0 = \langle\Psi_0|\hat{H}_1|\Psi_1\rangle - E_2 \tag{10}$$

The second order energy correction is the energy change associated with the first-order response of the wavefunction to the perturbation. Thus if Ψ_1 is known, then E_2 can be computed. In general, if the wavefunction response up to Ψ_n is known the energy corrections up to E_{2n+1} can be evaluated.

3 Møller–Plesset Perturbation Theory

Perturbation theory applied to the electronic Hamiltonian, using the Fock operator as the zeroth-order Hamiltonian is known as Møller–Plesset perturbation theory. Second-order Møller–Plesset perturbation theory (MP2) is a useful cost-effective method for the approximate treatment of electron correlation and is comparable in accuracy with density functional theory for structures and thermochemistry while also describing dispersive attractions.

The zeroth-order Hamiltonian is the Fock operator, which in second quantisation is the (diagonal) one-electron operator

$$\hat{F} = \sum_{pq} f_p^q a_q^\dagger a_p = \sum_p \epsilon_p a_p^\dagger a_p \tag{11}$$

Every configuration $|P\rangle$ is an eigenfunction of the Fock operator, with eigenvalue $\mathcal{E}_P$, the sum of the orbital eigenvalues of the spin-orbitals that comprise the configuration $|P\rangle$.

$$\hat{F}|P\rangle = \mathcal{E}_P|P\rangle \tag{12}$$

The zeroth-order wavefunction is the Hartree–Fock wavefunction $\Psi_0 = |0\rangle$. The perturbation is $\hat{H} - \hat{F}$ and applying the equations above the first-order energy correction is simply

$$E_1 = \langle 0|\hat{H}_1|0\rangle = \langle 0|\hat{H} - \hat{F}|0\rangle = E_{\text{HF}} - \mathcal{E}_0 \tag{13}$$

Thus, the Hartree–Fock energy is the sum of the zero- and first-order energies and is correct to first order in perturbation theory. To evaluate the second-order energy correction, we require the first-order wavefunction. We expand Ψ_1 using the full set of configurations $|P\rangle$, which form a complete basis for the second-quantised Hamiltonian.

$$(\hat{F} - \mathcal{E}_0)\sum_{P\neq 0} C_P^1|P\rangle = (E_1 - \hat{H} + \hat{F})\Psi_0 \tag{14}$$

Projecting on the left by a configuration $\langle Q|$ and integrating yeilds an equation that determines the contribution C_Q^1 of $|Q\rangle$ to Ψ_1

$$\sum_P C_P^1\langle Q|(\hat{F} - \mathcal{E}_0)|P\rangle = \langle Q|(E_1 - \hat{H} + \hat{F})|0\rangle \tag{15}$$

$$C_Q^1(\mathcal{E}_Q - \mathcal{E}_0) = -\langle Q|\hat{H}|0\rangle \tag{16}$$

From the point of view of the HF reference, $\hat{H}$ is a purely two-electron excitation operator and therefore the only non-zero C_Q^1 are those for doubly excited configurations $|{}^{ab}_{ij}\rangle$ so that

$$\Psi_1 = -\sum_{i>j,a>b} \frac{g_{ij}^{ab}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} |{}^{ab}_{ij}\rangle \tag{17}$$

The second-order energy has the simple form

$$E_2 = \sum_P C_P^1 \langle 0|(\hat{H} - \hat{F})|P\rangle \tag{18}$$

$$= -\sum_{i>j,a>b} \frac{g_{ij}^{ab} g_{ij}^{ab}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{19}$$

This is the MP2 correlation energy, associated with the first-order change of the Hartree–Fock wavefunction due to the Coulomb interaction of electrons. MP2 is a pair theory, where each pair correlates independently of the others. Both the wavefunction response Ψ_1 and the correlation energy decompose into contributions from every electron pair ij.

At n^{th} order in the perturbation, the energy as a function of the coupling strength

$$E_n(\lambda) = \sum_{i=0}^{n} E_i(\lambda)\lambda^i \tag{20}$$

Although the second order energy is almost always an improvement over the Hartree–Fock energy, the series is often oscillatory rather than monotonic. Moreover, convergence towards the FCI energy is not guaranteed. If there is a coupling strength $0 \le |\lambda| < 1$ for which an excited state becomes degenerate with the ground state, then the series will diverge. This is known as the intruder state problem. Consequently perturbation theory is not widely applied beyond second order corrections.

4 Goldstone Diagrams

The adiabatic connection of time-dependent perturbation theory is the formal connection between the exact groundstate wavefunction and the zeroth-order eigenstate state, where the connection is made by evolving with a time-dependent Hamiltonian in which the perturbation is switched on adiabatically slowly (Figure 1)

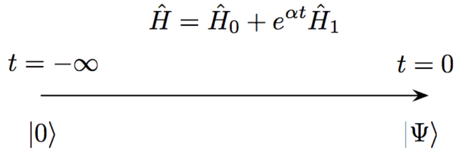


Figure 1: Turning on the perturbation adiabatically

The perturbation theory is performed with the Hamiltonian $\hat{H}_0 + e^{\alpha t}\hat{H}_1$ with small, positive α. At time $-\infty$ the non-interacting reference system is perfectly described by Hartree–Fock theory, and as time progresses towards $t = 0$ the system adiabatically transitions to the full, interacting system. Goldstone provided an elegant analysis of this process in which the limit $\alpha \to 0$ is taken, and time integrations are explicitly performed, to leave a time-independent many-body theory. Although the theory lacks time variables, traces of the original time-dependent formalism remain, particularly in terms of ordering events.

A detailed derivation is beyond this short course and is only sketched here. The Schrödinger equation can be cast into the following form

$$|\Psi\rangle = |0\rangle + (\mathcal{E}_0 - \hat{H}_0)^{-1}\hat{Q}(\hat{H}_1 + E_c)|\Psi\rangle \tag{21}$$

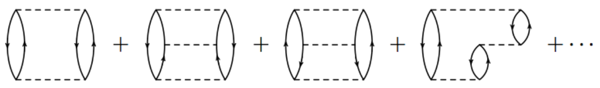
where $\hat{Q} = 1 - |0\rangle\langle 0|$ projects out the HF ground state. This is an iterative equation, where the left hand side can repeatedly be fed into the right hand side to convergence (if it converges). The result is a formally exact expression for the correlated (i.e. interacting) wavefunction and the corresponding exact energy

$$|\Psi\rangle = \sum_{n=0}^{\infty} \left(\frac{\hat{Q}}{\mathcal{E}_0 - \hat{H}_0} \hat{H}_1 \right)^n |0\rangle \tag{22}$$

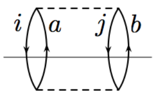
$$E = \mathcal{E}_0 + \sum_{n=0}^{\infty} \left\langle 0 \middle| \hat{H}_1 \left(\frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_1 \right)^n \middle| 0 \right\rangle \tag{23}$$

This is a perturbation series where the order of perturbation corresponds to how many times $\hat{H}_1$ appears. Goldstone devised a diagramatic representation of these equations using Feynman-like diagrams to organise the terms. In his notation, the diagramatic representation of the correlation energy is

$$E - E_{\mathrm{HF}} \;=$$



To explain these antisymmetrised Goldstone diagrams we will analyse just one of them in detail. The second-order diagram contains three key elements, illustrated below (recall that the HartreeFock energy is correct to first order in perturbation theory):



$\langle ab||ij\rangle$

$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}$

$\langle ij||ab\rangle$

The physical meaning of the various elements is as follows:

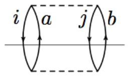
1. 'Time' progresses up the vertical axis (although there are no time variables)
2. The solid upwards lines denote particles (an electron in the virtual space)
3. The solid downward lines denotes holes (a hole in the occupied space)
4. The thin horizontal (resolvent) line corresponds to the energy denominator $(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}$ arising from $\hat{Q}/(E_0 - \hat{H}_0)$, which originates from the time propagators in the time-dependent theory.
5. The horizontal dashed lines refer to the perturbation, in this case, r_{ij}^{-1}.

The diagram can be read (from the bottom) as meaning that there is a spontaneous fluctuation of the reference system, caused by an interaction, in which one electron is excited $i \rightarrow a$ and another $j \rightarrow b$. The probability amplitude for this event is $\langle ij||ab\rangle/(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$. The process induces a change in the charge distribution whose energy is given by $\langle ab||ij\rangle$. Thus the whole term sums over all such events, scaling the electrostatic energy of the interaction by the probability amplitude of it happening.

We now move from general physical considerations to the detailed interpretation of Goldstone diagrams in terms of equations. To evaluate a closed antisymmetrised Goldstone diagram:

1. Label hole lines $i, j, k, \ldots$ and particle lines $a, b, c, \ldots$
2. Identify each 2-particle interaction line using the rule $\langle$ left-in right-in $||$ left-out right-out $\rangle$
3. Draw a resolvent line through all particle-hole lines after each interaction
4. Write down the product of all 2-electron integrals divided by the product of resolvents, and sum over all indices
5. Assign a phase $(-1)^{h-l}$ where h is the total number of hole lines and l the number of loops
6. Assign a factor 2^n where n is the number of equivalent pairs of particle or hole lines

Thus the second-order diagram above evaluates to



$$= \frac{1}{4}\sum_{ijab} \frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

which should be recognisable as the MP2 correlation energy. Each Goldstone diagram contributes at a specific order of perturbation theory, and the order is simply given by the number of 2-electron interaction lines.

Each resolvent line passes through some number of particle lines, and the same number of hole lines. The largest number of particle lines crossed by a resolvent line corresponds to the excitation order of the diagram. Coupled-cluster theory offers the means to sum all Goldstone diagrams (from all orders of perturbation theory) up to some particular excitation level and is the subject of L5.

5 Exercises

1. Write down the Hartree product and Hartree–Fock wavefunctions for triplet helium (configuration $1s\alpha 2s\alpha$) and work out the pair distribution function $P(\mathbf{r}_1, \mathbf{r}_2) = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2$. Identify the the contribution arising from Fermi correlation and hence show that the Coulomb repulsion between the two electrons is much less for the Hartree–Fock wavefunction than for the Hartree product wavefunction.

2. Use the technique of Lagrange multipliers to show that variationally minimising the CI energy is equivalent to solving the matrix eigenvalue problem $\mathbf{HC} = E\mathbf{C}$.

3. Apply the Slater–Condon rules to demonstrate that $\langle P|\hat{H}|0\rangle$ is zero unless the configuration $\langle P|$ is doubly excited with respect to the Hartree–Fock wavefunction $|0\rangle$.

4. Consider the perturbative treatment of a 2-state problem

$$\mathbf{H} = \begin{pmatrix} \alpha & \delta \\ \delta & \beta \end{pmatrix} \qquad \mathbf{H}_0 = \begin{pmatrix} \alpha + \alpha_s & 0 \\ 0 & \beta + \beta_s \end{pmatrix} \qquad \mathbf{H}_1 = \begin{pmatrix} -\alpha_s & \delta \\ \delta & -\beta_s \end{pmatrix} \tag{24}$$

   Obtain the eigenvalues of H in terms of the energy gap parameter $\epsilon = \beta - \alpha$ and the gap-shift parameter $\gamma = \beta_s - \alpha_s$. Show that the perturbation series diverges if

$$|\delta| > \frac{\epsilon}{2}\sqrt{1 + \frac{2\gamma}{\epsilon}} \tag{25}$$

   [JCP 112 9736 (2000)]

5. (Optionally) Write an MP2 code in Python using s- and p-type Gaussian orbitals on two atomic centres. Calculate the potential energy curve for helium dimer using the RHF and MP2 methods.