

Slides from FYS4411/FYS9411 Lectures

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Spring 2014

Topics for Week 3, January 13-17

Introduction, discussion of project and definitions

- ▶ Presentation of topics to be covered and definitions
- ▶ Discussion of the project and first steps
- ▶ Reading assignment for next week: study chapter 4 of Thijssen's text and chapter 7 of lectures notes of MHJ
- ▶ Computational assignment: solve numerically the one-body hydrogen-like problem (this week and next week).
- ▶ Form as soon as possible collaboration groups of 2-3 participants.

Course overview, Aims and Computational aspects

- ▶ The aim is to use the Hartree-Fock method to study atoms and molecules
- ▶ The results can be used to provide potentials and charge distributions for molecular dynamics simulations
- ▶ Eigenvalue solvers, efficient computations of integrals
- ▶ Iterative methods for solutions of non-linear equations
- ▶ Object orientation and efficient parallelization
- ▶ The first part of the project (ready by March 7) deals with Hartree-Fock calculations of closed-shell atoms like He, Be and Ne using standard hydrogen-like single-particle state functions.
- ▶ The second part includes optimized single-particle state functions and computations of both atoms and molecules

January 13 - May 31

Projects, deadlines and oral exam

1. Deadline part 1: March 7
2. Deadline full project: 31 May
3. Oral exam: To be settled

The oral exam is based on your presentation of the project.

More on projects

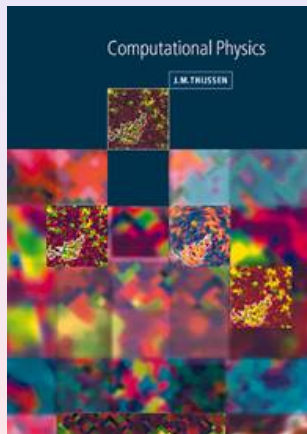
1. Keep a logbook, important for keeping track of all your changes etc etc.
2. The project should be written as a regular scientific article, with introduction, formalism, codes which have been developed and discussion of results. Conclusions and references should also be included. An example can be found on the webpage of the course.

The methods are relevant for atomic, molecular, solid state, materials science, life science, nanotechnology, quantum chemistry and nuclear physics.

Lectures and ComputerLab

- ▶ Lectures: Thursday (14.15-16, room FV329)
- ▶ Detailed lecture notes, all programs presented and projects can be found at the homepage of the course.
- ▶ Computerlab: 16-19 thursday, room FV329
- ▶ Weekly plans and relevant information are on the official webpage.
- ▶ Chapters 7 and 16 of the FYS3150 lecture notes give a good starting point. Chapter 16 will also be revised. We recommend also J. M. Thijssen text *Computational Physics*, chapters 3-6. For MPI we recommend Gropp, Lusk and Sjellum's text.

Thijssen's text



J. M. Thijssen's text






- ▶ Computational Physics
- ▶ Chapters 3-6
- ▶ **see** <http://www.tn.tudelft.nl/tn/People/Staff/Thijssen/comphybook.html>



Gropp, Lusk and Skjellum

- ▶ Using MPI
- ▶ Chapters 1-5
- ▶ see <http://mitpress.mit.edu/catalog/item/default.asp?tttype=2&tid=10761>

Selected Texts and lectures on C/C++

-  J. J. Barton and L. R. Nackman, *Scientific and Engineering C++*, Addison Wesley, 3rd edition 2000.
-  B. Stoustrup, *The C++ programming language*, Pearson, 1997.
-  George Em Karniadakis and Robert M. Kirby II, *Parallel Scientific Computing in C++ and MPI* <http://www.cambridge.org/catalogue/catalogue.asp?isbn=9780521520805>
-  D. Yang, *C++ and Object-oriented Numeric Computing for Scientists and Engineers*, Springer 2000.
-  More books reviewed at <http://www.accu.org/> and <http://www.comeaucomputing.com/booklist/>

Definitions

The quantum mechanical wave function of a given state with quantum numbers λ (encompassing all quantum numbers needed to specify the system), ignoring time, is with N particles (electrons in our case)

$$\Psi_\lambda = \Psi_\lambda(x_1, x_2, \dots, x_N),$$

with $x_i = (\mathbf{r}_i, \sigma_i)$ and the projection of σ_i takes the values $\{-1/2, +1/2\}$ for fermions with spin $1/2$. We will hereafter always refer to Ψ_λ as the exact wave function, and if the ground state is not degenerate we label it as

$$\Psi_0 = \Psi_0(x_1, x_2, \dots, x_N).$$

Definitions

Since the solution Ψ_λ seldomly can be found in closed form, approximations are sought. In this text we define an approximative wave function or an ansatz to the exact wave function as

$$\Phi_\lambda = \Phi_\lambda(x_1, x_2, \dots, x_N),$$

with

$$\Phi_0 = \Phi_0(x_1, x_2, \dots, x_N),$$

being the ansatz to the ground state.

Definitions

The wave function Ψ_λ is sought in the Hilbert space of either symmetric or anti-symmetric N -body functions, namely

$$\Psi_\lambda \in \mathcal{H}_N := \mathcal{H}_1 \oplus \mathcal{H}_1 \oplus \cdots \oplus \mathcal{H}_1,$$

where the single-particle Hilbert space \mathcal{H}_1 is the space of square integrable functions over $\mathbb{R}^d \oplus (\sigma)$ resulting in

$$\mathcal{H}_1 := L^2(\mathbb{R}^d \oplus (\sigma)).$$

Definitions

Our Hamiltonian is invariant under the permutation (interchange) of two fermions. Since we deal with fermions however, the total wave function is antisymmetric. Let \hat{P} be an operator which interchanges two fermions. Due to the symmetries we have ascribed to our Hamiltonian, this operator commutes with the total Hamiltonian,

$$[\hat{H}, \hat{P}] = 0,$$

meaning that $\Psi_\lambda(x_1, x_2, \dots, x_N)$ is an eigenfunction of \hat{P} as well, that is

$$\hat{P}_{ij}\Psi_\lambda(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N) = \beta\Psi_\lambda(x_1, x_2, \dots, x_j, \dots, x_i, \dots, x_N).$$

where β is the eigenvalue of \hat{P} . We have introduced the suffix ij in order to indicate that we permute fermions i and j . The Pauli principle tells us that the total wave function for a system of fermions has to be antisymmetric, resulting in the eigenvalue $\beta = -1$.

Definitions and notations

The Schrödinger equation reads

$$\hat{H}(x_1, x_2, \dots, x_N) \Psi_\lambda(x_1, x_2, \dots, x_N) = E_\lambda \Psi_\lambda(x_1, x_2, \dots, x_N), \quad (1)$$

where the vector x_i represents the coordinates (spatial and spin) of particle i , λ stands for all the quantum numbers needed to classify a given N -particle state and Ψ_λ is the pertaining eigenfunction. Throughout this course, Ψ refers to the exact eigenfunction, unless otherwise stated.

Definitions and notations

We write the Hamilton operator, or Hamiltonian, in a generic way

$$\hat{H} = \hat{T} + \hat{V}$$

where \hat{T} represents the kinetic energy of the system

$$\hat{T} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) = \sum_{i=1}^N t(x_i)$$

while the operator \hat{V} for the potential energy is given by

$$\hat{V} = \sum_{i=1}^N \hat{u}_{\text{ext}}(x_i) + \sum_{ji=1}^N v(x_i, x_j) + \sum_{ijk=1}^N v(x_i, x_j, x_k) + \dots \quad (2)$$

Hereafter we use natural units, viz. $\hbar = c = e = 1$, with e the elementary charge and c the speed of light. This means that momenta and masses have dimension energy.

Definitions and notations

If one does quantum chemistry or atomic physics as we do here, after having introduced the Born-Oppenheimer approximation which effectively freezes out the nucleonic degrees of freedom, the Hamiltonian for $N = n_e$ electrons takes the following form

$$\hat{H} = \sum_{i=1}^{n_e} t(x_i) - \sum_{i=1}^{n_e} k \frac{Z}{r_i} + \sum_{i < j}^{n_e} \frac{k}{r_{ij}},$$

with $k = 1.44 \text{ eVnm}$

Definitions and notations

We can rewrite this as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{n_e} \hat{h}_0(x_i) + \sum_{i < j=1}^{n_e} \frac{1}{r_{ij}}, \quad (3)$$

where we have defined $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and

$$\hat{h}_0(x_i) = \hat{t}(x_i) - \frac{Z}{x_i}. \quad (4)$$

The first term of eq. (3), H_0 , is the sum of the N *one-body* Hamiltonians \hat{h}_0 . Each individual Hamiltonian \hat{h}_0 contains the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, H_I , is the sum of the $n_e(n_e - 1)/2$ two-body interactions between each pair of electrons. Note that the double sum carries a restriction $i < j$.

Definitions and notations

The potential energy term due to the attraction of the nucleus defines the one-body field $u_i = u_{\text{ext}}(x_i)$ of Eq. (2). We have moved this term into the \hat{H}_0 part of the Hamiltonian, instead of keeping it in \hat{V} as in Eq. (2). The reason is that we will hereafter treat \hat{H}_0 as our non-interacting Hamiltonian. For a many-body wavefunction Φ_λ defined by an appropriate single-particle basis, we may solve exactly the non-interacting eigenvalue problem

$$\hat{H}_0 \Phi_\lambda = w_\lambda \Phi_\lambda,$$

with w_λ being the non-interacting energy. This energy is defined by the sum over single-particle energies to be defined below. For atoms the single-particle energies could be the hydrogen-like single-particle energies corrected for the charge Z . For nuclei and quantum dots, these energies could be given by the harmonic oscillator in three and two dimensions, respectively.

Definitions and notations

We will assume that the interacting part of the Hamiltonian can be approximated by a two-body interaction. This means that our Hamiltonian is written as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^N \hat{h}_0(x_i) + \sum_{i < j=1}^N \hat{v}(x_{ij}), \quad (5)$$

with

$$H_0 = \sum_{i=1}^N \hat{h}_0(x_i) = \sum_{i=1}^N \left(\hat{t}(x_i) + \hat{u}_{\text{ext}}(x_i) \right). \quad (6)$$

The one-body part $u_{\text{ext}}(x_i)$ is normally approximated by a harmonic oscillator potential or the Coulomb interaction an electron feels from the nucleus. However, other potentials are fully possible, such as one derived from the self-consistent solution of the Hartree-Fock equations or so-called Woods-Saxon potentials used in nuclear physics.

Definitions and notations

Our Hamiltonian is invariant under the permutation (interchange) of two fermions. Since we deal with fermions, the total wave function is antisymmetric. Let \hat{P} be an operator which interchanges two fermions. Due to the symmetries we have ascribed to our Hamiltonian, this operator commutes with the total Hamiltonian,

$$[\hat{H}, \hat{P}] = 0,$$

meaning that $\Psi_\lambda(x_1, x_2, \dots, x_N)$ is an eigenfunction of \hat{P} as well, that is

$$\hat{P}_{ij}\Psi_\lambda(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N) = \beta\Psi_\lambda(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N),$$

where β is the eigenvalue of \hat{P} . We have introduced the suffix ij in order to indicate that we permute fermions i and j . The Pauli principle tells us that the total wave function for a system of fermions has to be antisymmetric, resulting in the eigenvalue $\beta = -1$.

Definitions and notations

In our case we assume that we can approximate the exact eigenfunction with a Slater determinant

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \sigma) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\alpha(x_2) & \dots & \dots & \psi_\alpha(x_N) \\ \psi_\beta(x_1) & \psi_\beta(x_2) & \dots & \dots & \psi_\beta(x_N) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\sigma(x_1) & \psi_\sigma(x_2) & \dots & \dots & \psi_\sigma(x_N) \end{vmatrix}, \quad (7)$$

where x_i stand for the coordinates and spin values of a particle i and $\alpha, \beta, \dots, \gamma$ are quantum numbers needed to describe remaining quantum numbers.

Definitions and notations

Let us denote the ground state energy by E_0 . According to the variational principle we have

$$E_0 \leq E[\Phi] = \int \Phi^* \hat{H} \Phi d\tau$$

where Φ is a trial function which we assume to be normalized

$$\int \Phi^* \Phi d\tau = 1,$$

where we have used the shorthand $d\tau = d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$.

Definitions and notations

In the Hartree-Fock method the trial function is the Slater determinant of Eq. (7) which can be rewritten as

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \frac{1}{\sqrt{N!}} \sum_P (-)^P \hat{P} \psi_\alpha(x_1) \psi_\beta(x_2) \dots \psi_\nu(x_N) = \sqrt{N!} \mathcal{A} \Phi_H, \quad (8)$$

where we have introduced the antisymmetrization operator \mathcal{A} defined by the summation over all possible permutations of two fermions.

Definition and notations

Before we proceed, we need to discuss the single-particle states which enter the definition of the Slater determinant. We will start with hydrogen-like orbits and write a small program which diagonalizes the hydrogen-like problem. To achieve this, we need to refresh our knowledge about the Schrödinger equation for the hydrogen atom. To solve the Schrödinger equation as a matrix diagonalization problem, let us study the radial part of the Schrödinger equation. The radial part of the wave function, $R(r)$, is a solution to

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R(r) + V(r)R(r) = ER(r).$$

In our case $V(r) = -Z/r$.

Definition and notations

Then we substitute $R(r) = (1/r)u(r)$ and obtain

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + \left(V(r) + \frac{l(l+1)}{r^2} \frac{\hbar^2}{2m} \right) u(r) = Eu(r).$$

We introduce a dimensionless variable $\rho = (1/\alpha)r$ where α is a constant with dimension length and get

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{d\rho^2} u(\rho) + \left(V(\rho) + \frac{l(l+1)}{\rho^2} \frac{\hbar^2}{2m\alpha^2} \right) u(\rho) = Eu(\rho).$$

Definition and notations

We replace ρ with x , take away the centrifugal barrier (that is setting $l = 0$) term and set the potential equal to

$$V(x) = -\frac{kZ}{x\alpha},$$

with $k = 1.44$ eVnm being a constant. We multiply with $m\alpha^2/\hbar^2$ and since α is just a constant, we fix it by requiring that

$$\frac{kZm\alpha}{\hbar^2} = 1,$$

giving

$$\alpha = \frac{\hbar^2}{kZm},$$

which is the Bohr radius and leads to a natural length scale. This leads to the equation

$$-\frac{1}{2} \frac{d^2}{dx^2} u(x) - \frac{1}{x} u(x) = \lambda u(x),$$

with

$$\lambda = \frac{Em\alpha^2}{\hbar^2}.$$

Definition and notations

Let us now see how we can rewrite this equation as a matrix eigenvalue problem. First we need to compute the second derivative. We use here the following expression for the second derivative of a function f

$$f'' = \frac{f(x+h) - 2f(x) + f(x-h)}{h^2} + O(h^2),$$

where h is our step. Next we define minimum and maximum values for the variable x , R_{\min} and R_{\max} , respectively. With a given number of steps, N_{step} , we then define the step h as

$$h = \frac{R_{\max} - R_{\min}}{N_{\text{step}}}.$$

Definition and notations

We discretize x as

$$x_i = R_{\min} + ih \quad i = 1, 2, \dots, N_{\text{step}} - 1$$

we can rewrite the Schrödinger equation for x_i as

$$-\frac{1}{2} \frac{u(x_k + h) - 2u(x_k) + u(x_k - h))}{h^2} - \frac{1}{x_k} u(x_k) = \lambda u(x_k),$$

or in a more compact way

$$-\frac{1}{2} \frac{u_{k+1} - 2u_k + u_{k-1}}{h^2} - \frac{1}{x_k} u_k = -\frac{1}{2} \frac{u_{k+1} - 2u_k + u_{k-1}}{h^2} + V_k u_k = \lambda u_k,$$

where $u_k = u(x_k)$, $u_{k\pm 1} = u(x_k \pm h)$ and $V_k = -1/x_k$, the given potential.

Definition and notations

Let us see how this recipe may lead to a matrix reformulation of the Schrödinger equation. Define first the diagonal matrix element

$$d_k = \frac{1}{h^2} + V_k,$$

and the non-diagonal matrix element

$$e_k = -\frac{1}{2h^2}.$$

In this case the non-diagonal matrix elements are given by a mere constant. *All non-diagonal matrix elements are equal.* With these definitions the Schrödinger equation takes the following form

$$d_k u_k + e_{k-1} u_{k-1} + e_{k+1} u_{k+1} = \lambda u_k,$$

where u_k is unknown.

Definition and notations

Since we have N_{step} values of k we can write the latter equation as a matrix eigenvalue problem

$$\begin{pmatrix} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & d_{N_{\text{step}}-1} & e_{N_{\text{step}}-1} \\ 0 & \dots & \dots & \dots & \dots & e_{N_{\text{step}}-1} & d_{N_{\text{step}}} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{N_{\text{step}}} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{N_{\text{step}}} \end{pmatrix} \quad (9)$$

When setting up the matrix, be careful with the endpoints. Our wave function has the values $u(0) = u(\infty) = 0$ and you don't need to include these points in the equations.

Definition and notations

This is a matrix problem with a tridiagonal matrix of dimension $N_{\text{step}} \times N_{\text{step}}$ and will thus yield N_{step} eigenvalues.

The algorithm for solving this problem may take the following form

- ▶ Define values for N_{step} , R_{min} and R_{max} . These values define in turn the step size h . Typical values for R_{max} and R_{min} could be 0 and 10 respectively for the lowest-lying states. The number of mesh points N_{step} could be in the range 100 to some thousands. You can check the stability of the results as functions of N_{step} and R_{max} and R_{min} against the exact solutions.
- ▶ Construct then two one-dimensional arrays which contain all values of x_k and the potential V_k . For the latter it can be convenient to write a small function which sets up the potential as function of x_k . For the three-dimensional case you may also need to include the centrifugal potential.

Definition and notations

- ▶ Construct thereafter the one-dimensional vectors d and e , where d stands for the diagonal matrix elements and e the non-diagonal ones. Be careful with the endpoints, since we know the wave function u at both ends of the chosen grid.
- ▶ We are now ready to obtain the eigenvalues by calling the function *tqli* which can be found on the web page of the course FYS3150, see fall 2013. Calling *tqli*, you have to transfer the vectors d and e and their dimension $n = N_{\text{step}}$ and a matrix z of dimension $N_{\text{step}} \times N_{\text{step}}$ which returns the eigenfunctions. On return, the array d contains the eigenvalues. If z is given as the unity matrix on input, it returns the eigenvectors. For a given eigenvalue k , the eigenvector is given by the column k in z , that is $z[][k]$ in C, or $z(:,k)$ in Fortran.

Definition and notations

- ▶ TQLI does however not return an ordered sequence of eigenvalues. You may then need to sort them as e.g., an ascending series of numbers. The program we provide includes a sorting function as well.

This program is discussed in chapter 7 of the FYS3150 Lecture notes.

Definition and notations

- ▶ Your task this week and next week is to set up a program which solves the above problem.
- ▶ The program TQLI can be found in the lib.cpp (use also the lib.h file) at the webpage of FYS3150, click on the program link of the Fall 2013 version of the course. Read also chapter 7 of the FYS3150 Lectures.
- ▶ The eigenvalue for the lowest state should be $-1/2$ for the hydrogen-like problem. You should also plot the eigenvector. Compute also the second $l = 0$ state, both its energy and its eigenfunction.
- ▶ Try also to include the centrifugal barrier and find the lowest eigenstate and eigenvector for $l = 1$ and comment your results.
- ▶ At the lab, we will also discuss how to use armadillo instead of the standard memory allocation done in chapter 7.

Definitions and notations

It is defined as

$$\mathcal{A} = \frac{1}{N!} \sum_p (-)^p \hat{P}, \quad (10)$$

with p standing for the number of permutations. We have introduced for later use the so-called Hartree-function, defined by the simple product of all possible single-particle functions

$$\Phi_H(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \psi_\alpha(x_1) \psi_\beta(x_2) \dots \psi_\nu(x_N).$$

Definitions and notations

Both \hat{H}_0 and \hat{H} are invariant under all possible permutations of any two fermions and hence commute with \mathcal{A}

$$[H_0, \mathcal{A}] = [H_I, \mathcal{A}] = 0. \quad (11)$$

Furthermore, \mathcal{A} satisfies

$$\mathcal{A}^2 = \mathcal{A}, \quad (12)$$

since every permutation of the Slater determinant reproduces it.

Definitions and notations

The expectation value of \hat{H}_0

$$\int \Phi^* \hat{H}_0 \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_0 \mathcal{A} \Phi_H d\tau$$

is readily reduced to

$$\int \Phi^* \hat{H}_0 \Phi d\tau = N! \int \Phi_H^* \hat{H}_0 \mathcal{A} \Phi_H d\tau,$$

where we have used eqs. (11) and (12). The next step is to replace the antisymmetrization operator by its definition Eq. (8) and to replace \hat{H}_0 with the sum of one-body operators

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^N \sum_p (-)^p \int \Phi_H^* \hat{h}_0 \hat{P} \Phi_H d\tau.$$

Definitions and notations

The integral vanishes if two or more fermions are permuted in only one of the Hartree-functions Φ_H because the individual single-particle wave functions are orthogonal. We obtain then

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^N \int \Phi_H^* \hat{h}_0 \Phi_H d\tau.$$

Orthogonality of the single-particle functions allows us to further simplify the integral, and we arrive at the following expression for the expectation values of the sum of one-body Hamiltonians

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^N \int \psi_{\mu}^*(\mathbf{x}) \hat{h}_0 \psi_{\mu}(\mathbf{x}) d\mathbf{x}. \quad (13)$$

Definitions and notations

We introduce the following shorthand for the above integral

$$\langle \mu | \hat{h}_0 | \mu \rangle = \int \psi_\mu^*(\mathbf{x}) \hat{h}_0 \psi_\mu(\mathbf{x}) d\mathbf{x},$$

and rewrite Eq. (13) as

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^N \langle \mu | \hat{h}_0 | \mu \rangle. \quad (14)$$

Definitions and notations

The expectation value of the two-body part of the Hamiltonian (assuming a two-body Hamiltonian at most) is obtained in a similar manner. We have

$$\int \Phi^* \hat{H}_I \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_I \mathcal{A} \Phi_H d\tau,$$

which reduces to

$$\int \Phi^* \hat{H}_I \Phi d\tau = \sum_{i \leq j=1}^N \sum_p (-)^p \int \Phi_H^* \hat{v}(x_{ij}) \hat{P} \Phi_H d\tau,$$

by following the same arguments as for the one-body Hamiltonian.

Definitions and notations

Because of the dependence on the inter-particle distance r_{ij} , permutations of any two fermions no longer vanish, and we get

$$\int \Phi^* \hat{H}_I \Phi d\tau = \sum_{i < j=1}^N \int \Phi_H^* \hat{v}(x_{ij}) (1 - P_{ij}) \Phi_H d\tau.$$

where P_{ij} is the permutation operator that interchanges particle i and particle j . Again we use the assumption that the single-particle wave functions are orthogonal.

Definitions and notations

We obtain

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \left[\int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) \hat{v}(x_{ij}) \psi_{\mu}(x_i) \psi_{\nu}(x_j) dx_i dx_j \right. \\ \left. - \int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) \hat{v}(x_{ij}) \psi_{\nu}(x_i) \psi_{\mu}(x_j) dx_i dx_j \right]. \quad (15)$$

The first term is the so-called direct term. In Hartree-Fock theory it leads to the so-called Hartree term, while the second is due to the Pauli principle and is called the exchange term and in Hartree-Fock theory it defines the so-called Fock term. The factor 1/2 is introduced because we now run over all pairs twice.

Definitions and notations

The last equation allows us to introduce some further definitions. The single-particle wave functions $\psi_\mu(\mathbf{x})$, defined by the quantum numbers μ and \mathbf{x} (recall that \mathbf{x} also includes spin degree, later we will also add isospin) are defined as the overlap

$$\psi_\alpha(x) = \langle x | \alpha \rangle.$$

Definitions and notations

We introduce the following shorthands for the above two integrals

$$\langle \mu\nu | V | \mu\nu \rangle = \int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) \hat{V}(x_{ij}) \psi_{\mu}(x_i) \psi_{\nu}(x_j) dx_i dx_j,$$

and

$$\langle \mu\nu | V | \nu\mu \rangle = \int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) \hat{V}(x_{ij}) \psi_{\nu}(x_i) \psi_{\mu}(x_j) dx_i dx_j.$$

Definitions and notations

The direct and exchange matrix elements can be brought together if we define the antisymmetrized matrix element

$$\langle \mu\nu | V | \mu\nu \rangle_{\text{AS}} = \langle \mu\nu | V | \mu\nu \rangle - \langle \mu\nu | V | \nu\mu \rangle,$$

or for a general matrix element

$$\langle \mu\nu | V | \sigma\tau \rangle_{\text{AS}} = \langle \mu\nu | V | \sigma\tau \rangle - \langle \mu\nu | V | \tau\sigma \rangle.$$

It has the symmetry property

$$\langle \mu\nu | V | \sigma\tau \rangle_{\text{AS}} = -\langle \mu\nu | V | \tau\sigma \rangle_{\text{AS}} = -\langle \nu\mu | V | \sigma\tau \rangle_{\text{AS}}.$$

Definitions and notations

The antisymmetric matrix element is also hermitian, implying

$$\langle \mu\nu | V | \sigma\tau \rangle_{AS} = \langle \sigma\tau | V | \mu\nu \rangle_{AS}.$$

With these notations we rewrite Eq. (15) as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \langle \mu\nu | V | \mu\nu \rangle_{AS}. \quad (16)$$

Definitions and notations

Combining Eqs. (14) and (16) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^N \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \langle \mu \nu | V | \mu \nu \rangle_{\text{AS}}. \quad (17)$$

This equation is very useful, in particular if we only look at the unperturbed part H_0 .

This part can be represented by closed form expressions that can be used to check our algorithms.