

Appendix A

Solution of time-dependent Schrödinger equations

When the potential does not contain any explicit dependence upon time, the solution of time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = H\psi(x, t), \quad H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (\text{A.1})$$

for the one-dimensional case, can be obtained via variable separation and written down in terms of eigenvectors and eigenvalues of the time-independent Schrödinger equation, $H\psi_n(x) = E_n\psi_n(x)$, as

$$\psi(x, t) = \sum_n c_n e^{-iE_n t/\hbar} \psi_n(x), \quad c_n = \int \psi(x, 0) \psi_n^*(x) dx. \quad (\text{A.2})$$

The coefficients c_n guarantee that the system at $t = 0$ is in the desired state. One can formally write time evolution via an operator $U(t)$:

$$\psi(x, t) = U(t)\psi(x, 0), \quad U(t) = e^{-iHt/\hbar}, \quad (\text{A.3})$$

where the “exponential of an operator” is defined via the series expansion

$$e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!}. \quad (\text{A.4})$$

The time-evolution operator is *unitary*: $U^\dagger(t) = U^{-1}(t)$, and $U(-t) = U^\dagger(t)$ hold. These properties reflect important features of time evolution in quantum mechanics: it is *invariant under time reversal* and *conserves the norm*.

If the potential has an explicit dependence upon the time, variable separation is no longer possible. Analytical solutions of course exist only for a small number of cases. Let us consider the numerical solution of the time-dependent Schrödinger equation. This can be useful also for time-independent potentials, actually, since it may be more convenient to compute the time evolution for a given initial state than to project it over all eigenfunctions.

A.1 Discretization in time: Crank-Nicolson algorithm

Let us consider for simplicity the one-dimensional case. We first discretize the Laplacian operator on a uniform grid of N points x_i , as in Eq.(1.27):

$$\frac{d^2\psi}{dx^2} \equiv \frac{\psi_{i-1} + \psi_{i+1} - 2\psi_i}{(\Delta x)^2}, \quad \psi_i \equiv \psi(x_i, t). \quad (\text{A.5})$$

The right-hand side of the Schrödinger equation:

$$i\hbar \frac{\partial \psi_i}{\partial t} = -\frac{\hbar^2}{2m} \frac{\psi_{i-1} + \psi_{i+1} - 2\psi_i}{(\Delta x)^2} + V_i \psi_i, \quad V_i \equiv V(x_i) \quad (\text{A.6})$$

can be recast into a matrix-vector product:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (\text{A.7})$$

where ψ is the vector formed by the N values ψ_i , the $N \times N$ matrix H has the following nonzero terms ¹ only:

$$H = \begin{pmatrix} H_{1,1} & H_{1,2} & 0 & \dots & 0 \\ H_{2,1} & H_{2,2} & H_{2,3} & 0 & \vdots \\ 0 & H_{3,2} & H_{3,3} & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & H_{N-1,N} \\ 0 & \dots & 0 & H_{N,N-1} & H_{N,N} \end{pmatrix} \quad (\text{A.8})$$

where

$$H_{i,i} = \frac{\hbar^2}{m(\Delta x)^2} + V_i, \quad H_{i,i+1} = H_{i+1,i} = -\frac{\hbar^2}{2m(\Delta x)^2}. \quad (\text{A.9})$$

Let us now proceed to discretize in time, with "time step" Δt . The simplest algorithm one can think of is *Euler* discretization. One writes for the first derivative:

$$\frac{\partial \psi_i}{\partial t} \simeq \frac{\psi_i(t + \Delta t) - \psi_i(t)}{\Delta t} \quad (\text{A.10})$$

and derives the following equation ("forward" Euler) for the wave function at time $t + \Delta t$, given the wave function at time t :

$$\psi(t + \Delta t) = \psi(t) - \frac{i\Delta t}{\hbar} H\psi(t). \quad (\text{A.11})$$

From wave functions at each time step, one directly obtains wave functions at the following time step: the algorithm is thus *explicit*. Unfortunately it turns out that such algorithm is also numerically unstable (that is: it has solutions that grow exponentially with time, even when there aren't any such solutions in the original equation).

¹A matrix having such form is called *tridiagonal*.

A numerically stable algorithm is instead provided by the "backward" Euler discretization (notice the different time at the right-hand side):

$$\psi(t + \Delta t) = \psi(t) - \frac{i\Delta t}{\hbar} H \psi(t + \Delta t). \quad (\text{A.12})$$

This algorithm is called *implicit* because the wave function at the next time step cannot be simply obtained from the wave function at the previous one (note that the former appear in both sides of the equation). The discretized equations can however be recast into the form of a *linear system*:

$$A\psi(t + \Delta t) \equiv \left(1 + \frac{i\Delta t}{\hbar} H\right) \psi(t + \Delta t) = \psi(t). \quad (\text{A.13})$$

Since the matrix A is tridiagonal, its solution can be found very quickly, in order $\mathcal{O}(N)$ operations. The implicit Euler algorithm can be demonstrated to be numerically stable, but it still suffers from a major drawback: it breaks (with error proportional to the time step) the unitarity of the time evolution.

The better *Crank-Nicolson* algorithm is obtained by combining explicit and implicit Euler discretization:

$$\left(1 + \frac{i\Delta t}{2\hbar} H\right) \psi(t + \Delta t) = \left(1 - \frac{i\Delta t}{2\hbar} H\right) \psi(t) \quad (\text{A.14})$$

(notice the factor 2 dividing the time step: you can obtain the above formula by performing an explicit step, followed by an implicit one, both with time step $\Delta t/2$). This often used algorithm conserves unitarity of the time evolution up to order $\mathcal{O}((\Delta t)^2)$ and is numerically stable.

A.2 Direct discretization of the time evolution operator

As mentioned above, even for time-independent problems there are cases in which the solution via eigenvalues and eigenvectors is not practical, either because too many states are needed, or because their calculation is expensive. In these cases, the direct discretization of the time evolution operator $U(t)$, Eq.(A.3) may provide a convenient alternative.

Let us first decompose the Hamiltonian into kinetic and a potential energy, $H = T + V$. In general, one cannot decompose the exponential of the sum of two noncommuting operators into the product of two exponentials for each operator:

$$e^{(A+B)t} \neq e^{At}e^{Bt}, \quad [A, B] \neq 0. \quad (\text{A.15})$$

One can however use the *Trotter* formula, stating that

$$\lim_{n \rightarrow \infty} \left(e^{(A+B)t/n}\right)^n = \left(e^{At/n}e^{Bt/n}\right)^n. \quad (\text{A.16})$$

For finite n , the error is $\mathcal{O}((\Delta t)^2)$, where $\Delta t = t/n$. The discretization of the time evolution operator follows naturally:

$$e^{-iHt/\hbar} \simeq (U_T(\Delta t)U_V(\Delta t))^n, \quad (\text{A.17})$$

where the right-hand side is a sequence of applications of the time evolution operator, each consisting of the application of a purely potential term, followed by a purely kinetic one,

$$U_T(\Delta t) = e^{-iT\Delta t/\hbar}, \quad U_V(\Delta t) = e^{-iV\Delta t/\hbar}. \quad (\text{A.18})$$

The Trotter approximation would be of limited use without a simple way to calculate the two operators U_T and U_V . The former is hardly a problem, since the potential is a *diagonal* operator in real space (at least for a potential having the usual $V(r)$ form, i.e. a local potential). The application of U_V to a wave function on a real-space grid amounts to a simple multiplication:

$$U_V(\Delta t)\psi_i(t) = e^{-iV_i\Delta t/\hbar}\psi_i(t). \quad (\text{A.19})$$

In real space and in one dimension, the kinetic term is represented by a tridiagonal matrix like the one in Eq.(A.8) (without the potential contribution in the diagonal). The exponential of such an operator is far from simple (see its definition!). One can however take advantage of the Fast Fourier-Transform (FFT) algorithm to switch back and forth between real and Fourier (or “reciprocal”) space. In reciprocal space, the kinetic energy is diagonal and the calculation of $U(t)$ is trivial:

$$U_T(\Delta t)\tilde{\psi}_j(t) = e^{-i\hbar q_j^2 \Delta t/2m}\tilde{\psi}_j(t) \quad (\text{A.20})$$

where $\tilde{\psi}_j(t)$ is the Fourier transform of $\psi_i(t)$ of wave-vector q_j .

Appendix B

More on real-space grids

Let us consider again the one-dimensional time-independent Schrödinger equation, with the simplest discretization of the Laplacian operator for a uniform grid of N points x_i , Eq.(A.5). The resulting discretized Schrödinger equation can be recast under the form of a matrix equation:

$$\sum_{j=1}^N H_{ij} \psi_j = E \psi_i, \quad i = 1, N \quad (\text{B.1})$$

where the $N \times N$ matrix H is tridiagonal, with the nonzero terms given in Eq.(A.9). The resemblance with the secular equation as obtained from the variational principle is quite obvious, and can be made more explicit by introducing a set of “basis functions” $b_i(x)$ so defined:

$$b_i(x) = \frac{1}{\sqrt{\Delta x}} \quad x_i - \frac{\Delta x}{2} < x < x_i + \frac{\Delta x}{2} \quad (\text{B.2})$$

$$b_i(x) = 0 \quad x < x_i - \frac{\Delta x}{2}, x > x_i + \frac{\Delta x}{2}. \quad (\text{B.3})$$

It is straightforward to verify that these functions are orthonormal. The H_{ij} elements are the “matrix elements” of the Hamiltonian. The potential is represented by its value in the grid point: $V_{ii} = \langle b_i | V | b_i \rangle \simeq V(x_i)$ and is thus *diagonal* in this basis. The kinetic energy is less obvious: our basis functions are not differentiable, but the matrix elements for the kinetic energy:

$$T_{ij} = \langle b_i | T | b_j \rangle = -\frac{\hbar^2}{2m} \int b_i(x) \frac{d^2}{dx^2} b_j(x) dx \quad (\text{B.4})$$

can be specified via the discretized form of the second derivative, as in Eq.(A.5) for instance.

The solution of the Schrödinger equation via the secular equation is an alternative to numerical integration of Ch.1–3. In one dimension there is no special advantage in the former procedure, but in more dimensions this is the method of choice. The generalization to two and three dimensions is straightforward: for instance, we can introduce a uniform grid in the following way:

$$\vec{r}_{i,j,k} = (x_i, y_j, z_k), \quad x_i = i\Delta x, \quad y_j = j\Delta y, \quad z_k = k\Delta z. \quad (\text{B.5})$$

Assuming to solve our problem in a parallelepiped spanned by N_1, N_2, N_3 points along x, y, z respectively, we have $N = N_1 \cdot N_2 \cdot N_3$. The size of the computational problem may become quickly intractable. It should however be remarked that the Hamiltonian matrix is *sparse*: the potential is present only in the diagonal terms, while the kinetic energy has nonzero matrix elements only for a few points close to the one considered. The discretization of Eq.(A.5) generalizes in three dimensions to

$$\begin{aligned}\nabla^2\psi &\equiv \frac{\psi_{i-1,j,k} + \psi_{i+1,j,k} - 2\psi_{i,j,k}}{(\Delta x)^2} \\ &+ \frac{\psi_{i,j-1,k} + \psi_{i,j+1,k} - 2\psi_{i,j,k}}{(\Delta y)^2} \\ &+ \frac{\psi_{i,j,k-1} + \psi_{i,j,k+1} - 2\psi_{i,j,k}}{(\Delta z)^2},\end{aligned}\tag{B.6}$$

where $\psi_{i,j,k} = \psi(\vec{r}_{i,j,k})$ with $\vec{r}_{i,j,k}$ as in Eq.(B.5). More accurate (higher-order) finite-difference formulae for the Laplacian can be in principle (and are in practice) used, but they all share the same characteristics: they use only a few points around the one for which we want to calculate the Laplacian. Sparseness is very often the key to fast solution.

Appendix C

The Helium atom

C.1 Perturbative treatment for Helium atom

The Helium atom is characterized by a Hamiltonian operator

$$H = -\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{Zq_e^2}{r_1} - \frac{\hbar^2 \nabla_2^2}{2m_e} - \frac{Zq_e^2}{r_2} + \frac{q_e^2}{r_{12}} \quad (\text{C.1})$$

where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ is the distance between the two electrons. The last term corresponds to the Coulomb repulsion between the two electrons and makes the problem non separable.

As a first approximation, let us consider the interaction between electrons:

$$V = \frac{q_e^2}{r_{12}} \quad (\text{C.2})$$

as a perturbation to the problem described by

$$H_0 = -\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{Zq_e^2}{r_1} - \frac{\hbar^2 \nabla_2^2}{2m_e} - \frac{Zq_e^2}{r_2} \quad (\text{C.3})$$

which is easy to solve since it is separable into two independent problems of a single electron under a central Coulomb field, i.e. a Hydrogen-like problem with nucleus charge $Z = 2$. The ground state for this system is given by the wave function described in Eq.(2.29) (1s orbital):

$$\phi^0(\mathbf{r}_i) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr_i} \quad (\text{C.4})$$

in a.u.. We note that we can assign to both electrons the same wave function, as long as their spin is opposite. The total unperturbed wave function (coordinate part) is simply the product

$$\psi^0(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \quad (\text{C.5})$$

which is a symmetric function (antisymmetry being provided by the spin part). The energy of the corresponding ground state is the sum of the energies of the two Hydrogen-like atoms:

$$E_0 = -2Z^2 \text{Ry} = -8 \text{Ry} \quad (\text{C.6})$$

since $Z = 2$. The electron repulsion will necessarily raise this energy, i.e. make it less negative. In first-order perturbation theory,

$$E - E_0 = \langle \psi_0 | V | \psi_0 \rangle \quad (\text{C.7})$$

$$= \frac{Z^6}{\pi^2} \int \frac{2}{r_{12}} e^{-2Z(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (\text{C.8})$$

$$= \frac{5}{4} Z \text{ Ry}. \quad (\text{C.9})$$

For $Z = 2$ the correction is equal to 2.5 Ry and yields $E = -8 + 2.5 = -5.5$ Ry. The experimental value is -5.8074 Ry. The perturbative approximation is not accurate but provides a reasonable estimate of the correction, even if the “perturbation”, i.e. the Coulomb repulsion between electrons, is of the same order of magnitude of all other interactions. Moreover, the ground state assumed in perturbation theory is usually qualitatively correct: the exact wave function for He will be close to a product of two 1s functions.

C.2 Variational treatment for Helium atom

The Helium atom provides a simple example of application of the variational method. The independent-electron solution, Eq.(C.5), is missing the phenomenon of *screening*: each electron will “feel” a nucleus with partially screened charge, due to the presence of the other electron. In order to account for this phenomenon, we may take as our trial wave function an expression like the one of Eq.(C.5), with the true charge of the nucleus Z replaced by an “effective charge” Z_e , presumably smaller than Z . Let us find the optimal Z_e variationally, i.e. by minimizing the energy. We assume

$$\psi(\mathbf{r}_1, \mathbf{r}_2; Z_e) = \frac{Z_e^3}{\pi} e^{-Z_e(r_1+r_2)} \quad (\text{C.10})$$

and we re-write the Hamiltonian as:

$$H = \left[-\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{Z q_e^2}{r_1} - \frac{\hbar^2 \nabla_2^2}{2m_e} - \frac{Z q_e^2}{r_2} \right] + \left[-\frac{(Z - Z_e) q_e^2}{r_1} - \frac{(Z - Z_e) q_e^2}{r_2} + \frac{q_e^2}{r_{12}} \right] \quad (\text{C.11})$$

We now calculate

$$E(Z_e) = \int \psi^*(\mathbf{r}_1, \mathbf{r}_2; Z_e) H \psi(\mathbf{r}_1, \mathbf{r}_2; Z_e) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (\text{C.12})$$

The contribution to the energy due to the first square bracket in Eq.(C.11) is $-2Z_e^2$ a.u.: this is in fact a Hydrogen-like problem for a nucleus with charge Z_e , for two non-interacting electrons. By expanding the remaining integrals and using symmetry we find

$$E(Z_e) = -2Z_e^2 - \int |\psi|^2 \frac{4(Z - Z_e)}{r_1} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \int |\psi|^2 \frac{2}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (\text{C.13})$$

(in a.u.) with

$$|\psi|^2 = \frac{Z_e^6}{\pi^2} e^{-2Z_e(r_1+r_2)} \quad (\text{C.14})$$

Integrals can be easily calculated and the result is

$$E(Z_e) = -2Z_e^2 - 4(Z - Z_e)Z_e + 2\frac{5}{8}Z_e = 2Z_e^2 - \frac{27}{4}Z_e \quad (\text{C.15})$$

where we explicitly set $Z = 2$. Minimization of $E(Z_e)$ with respect to Z_e immediately leads to

$$Z_e = \frac{27}{16} = 1.6875 \quad (\text{C.16})$$

and the corresponding energy is

$$E = -\frac{729}{128} = -5.695 \text{ Ry} \quad (\text{C.17})$$

This result is definitely better than the perturbative result $E = -5.50 \text{ Ry}$, even if there is still a non-negligible distance with the experimental result $E = -5.8074 \text{ Ry}$.

It is possible to improve the variational result by extending the set of trial wave functions. Sect.(7.1) shows how to produce the best single-electron functions using the Hartree-Fock method. Even better results can be obtained using trial wave functions that are more complex than a simple product of single-electron functions. For instance, let us consider trial wave functions like

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = [f(\mathbf{r}_1)g(\mathbf{r}_2) + g(\mathbf{r}_1)f(\mathbf{r}_2)], \quad (\text{C.18})$$

where the two single-electron functions, f and g , are Hydrogen-like wave function as in Eq.(C.4) with different values of Z , that we label Z_f and Z_g . By minimizing with respect to the two parameters Z_f and Z_g , one finds $Z_f = 2.183$, $Z_g = 1.188$, and an energy $E = -5.751 \text{ Ry}$, much closer to the experimental result than for a single effective Z . Note that the two functions are far from being similar!

C.3 ”Exact” treatment for Helium atom

Let us make no explicit assumption on the form of the ground-state wave function of He. We assume however that the total spin is zero and thus the coordinate part of the wave function is symmetric. The wave function is expanded over a suitable basis set, in this case a symmetrized product of two single-electron gaussians. The lower-energy wave function is found by diagonalization. Such approach is of course possible only for a very small number of electrons.

Code `helium_gauss.f90`¹ (or `helium_gauss.c`²) looks for the ground state of the He atom, using an expansion into Gaussian functions, already introduced in the code `hydrogen_gauss`. We assume that the solution is the product of a symmetric coordinate part and of an antisymmetric spin part, with total spin $S = 0$. The coordinate part is expanded into a basis of symmetrized products of gaussians, B_k :

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k c_k B_k(\mathbf{r}_1, \mathbf{r}_2). \quad (\text{C.19})$$

¹http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/F90/helium_gauss.f90

²http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/C/helium_gauss.c

If the b_i functions are S-like gaussians as in Eq.(5.22), we have:

$$B_k(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(b_{i(k)}(\mathbf{r}_1) b_{j(k)}(\mathbf{r}_2) + b_{i(k)}(\mathbf{r}_2) b_{j(k)}(\mathbf{r}_1) \right) \quad (\text{C.20})$$

where k is an index running over $n(n+1)/2$ pairs $i(k), j(k)$ of gaussian functions. The overlap matrix $\tilde{S}_{kk'}$ may be written in terms of the S_{ij} overlap matrices, Eq.(5.25), of the hydrogen-like case:

$$\tilde{S}_{kk'} = \langle B_k | B_{k'} \rangle = (S_{ii'} S_{jj'} + S_{ij'} S_{ji'}) . \quad (\text{C.21})$$

The matrix elements, $\tilde{H}_{kk'}$, of the Hamiltonian:

$$\tilde{H}_{kk'} = \langle B_k | H | B_{k'} \rangle, \quad H = -\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{Z q_e^2}{r_1} - \frac{\hbar^2 \nabla_2^2}{2m_e} - \frac{Z q_e^2}{r_2} + \frac{q_e^2}{r_{12}} \quad (\text{C.22})$$

can be written using matrix elements $H_{ij} = H_{ij}^K + H_{ij}^V$, obtained for the hydrogen-like case with $Z = 2$, Eq.(5.26) and (5.27):

$$\tilde{H}_{kk'} = (H_{ii'} S_{jj'} + H_{ij'} S_{ji'} + S_{ii'} H_{jj'} + H_{ij'} S_{ji'}) + \langle B_k | V_{ee} | B_{k'} \rangle, \quad (\text{C.23})$$

and the matrix element of the Coulomb electron-electron interaction V_{ee} :

$$\begin{aligned} \langle B_k | V_{ee} | B_{k'} \rangle &= \int b_{i(k)}(\mathbf{r}_1) b_{j(k)}(\mathbf{r}_2) \frac{q_e^2}{r_{12}} b_{i(k')}(\mathbf{r}_1) b_{j(k')}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &+ \int b_{i(k)}(\mathbf{r}_1) b_{j(k)}(\mathbf{r}_2) \frac{q_e^2}{r_{12}} b_{j(k')}(\mathbf{r}_1) b_{i(k')}(\mathbf{r}_2) d^3 r_1 d^3 r_2. \end{aligned} \quad (\text{C.24})$$

These matrix elements can be written, using Eq.(7.33), as

$$\langle B_k | V_{ee} | B_{k'} \rangle = \frac{q_e^2 \pi^{5/2}}{\alpha \beta (\alpha + \beta)^{1/2}} + \frac{q_e^2 \pi^{5/2}}{\alpha' \beta' (\alpha' + \beta')^{1/2}}, \quad (\text{C.25})$$

where

$$\alpha = \alpha_{i(k)} + \alpha_{i(k')}, \quad \beta = \alpha_{j(k)} + \alpha_{j(k')}, \quad \alpha' = \alpha_{i(k)} + \alpha_{j(k')}, \quad \beta' = \alpha_{j(k)} + \alpha_{i(k')}. \quad (\text{C.26})$$

In an analogous way one can calculate the matrix elements between symmetrized products of gaussians formed with P-type gaussian functions (those defined in Eq.5.23). The combination of P-type gaussians with $L = 0$ has the form:

$$B_k(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\mathbf{r}_1 \cdot \mathbf{r}_2) \left(b_{i(k)}(\mathbf{r}_1) b_{j(k)}(\mathbf{r}_2) + b_{i(k)}(\mathbf{r}_2) b_{j(k)}(\mathbf{r}_1) \right) \quad (\text{C.27})$$

It is immediately verified that the product of a S-type and a P-type gaussian yields an odd function that does not contribute to the ground state.

In the case with S-type gaussians only, the code writes to file "gs-wfc.out" the function:

$$P(r_1, r_2) = (4\pi r_1 r_2)^2 |\psi(r_1, r_2)|^2, \quad (\text{C.28})$$

where $P(r_1, r_2)dr_1dr_2$ is the joint probability to find an electron between r_1 and $r_1 + dr_1$, and an electron between r_2 and $r_2 + dr_2$. The probability to find an electron between r and $r + dr$ is given by $p(r)dr$, with

$$p(r) = 4\pi r^2 \int |\psi(r, r_2)|^2 4\pi r_2^2 dr_2 = \int P(r, r_2) dr_2. \quad (\text{C.29})$$

It is easy to verify that for a wave function composed by a product of two identical functions, like the one in (C.5), the joint probability is the product of single-electron probabilities: $P(r_1, r_2) = p(r_1)p(r_2)$. This is not true in general for the exact wave function.

C.4 Laboratory

- observe the effect of the number of basis functions, to the choice of coefficients λ of the gaussians, to the inclusion of P-type gaussians
- compare the obtained energy with the one obtained by other methods: perturbation theory with hydrogen-like wave functions, (Sec.C.1), variational theory with effective Z (Sec.C.2), exact result (-5.8074 Ry).
- Make a plot of the probability $P(r_1, r_2)$ and of the difference $P(r_1, r_2) - p(r_1)p(r_2)$, using for instance **gnuplot** and the following commands:

```
set view 0, 90
unset surface
set contour
set cntrparam levels auto 10
splot [0:4][0:4] "gs-wfc.out" u 1:2:3 w l
```

Note that the probability $P(r_1, r_2)$ (column 3 in "splot") is not exactly equal to the product $p(r_1)p(r_2)$ (column 4; column 5 is the difference between the two).