Some notes on non-interacting systems and density matrices

We consider a non-interacting system of particles with Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + v(\bar{r}_i) = \sum_{i=1}^{N} h(\bar{r}_i) \qquad (1)$$

where we defined

$$h(\bar{r}) = -\frac{1}{2}\nabla^2 + v(\bar{r}) \qquad (2)$$

We want to construct the fermionic eigenstates of (1), i.e. wavefunctions satisfying

$$\Psi(\dots x_i \dots x_j \dots) = -\Psi(\dots x_j \dots x_i \dots)$$

$x_i = (\bar{r}_i, \sigma_i)$ space-spin variable

Let $\varphi_i(\bar{r},\sigma)$ be a complete set of eigenstates of the one-particle Hamiltonian (2), then:

$$h(\bar{r})\varphi_i(\bar{r},\sigma) = \epsilon_i \varphi_i(\bar{r},\sigma) \qquad (3)$$

$$\langle \varphi_i | \varphi_j \rangle = \int dx\, \varphi_i^*(x)\varphi_j(x) = \delta_{ij} \qquad (4)$$

$$\int dx = \sum_\sigma \int d\bar{r}$$

Then the fermionic eigenstates of (1) are given by

$$\Psi_I = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{i_1}(x_1) & \cdots & \varphi_{i_N}(x_1) \\ \vdots & & \vdots \\ \varphi_{i_1}(x_N) & \cdots & \varphi_{i_N}(x_N) \end{vmatrix} \qquad (5)$$

where $I = (i_1, \dots, i_N)$, $i_1 < \dots < i_N$

These form a complete and orthonormal set of eigenstates as we will show next.

Let us check that (5) is an eigenstate of (1).
We start be considering the explicit form of the determinant.

$$\Psi_I = \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\operatorname{sgn}\sigma} \varphi_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_N)}(x_N) \qquad (6)$$

where we sum over all permutations σ of N-elements and σ is the sign of the permutation.
(For example for $\sigma(123) = (213)$, we have $\operatorname{sgn}\sigma = -1$)

Then

$$\hat{H}\Psi_I = \frac{1}{\sqrt{N!}} \sum_{\sigma} \left(h(\bar{r}_1) + \cdots + h(\bar{r}_N)\right) (-1)^{\operatorname{sgn}\sigma} \varphi_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_N)}(x_N)$$

$$= \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\operatorname{sgn}\sigma} \Big\{ \left(h(r_1)\varphi_{\sigma(i_1)}(x_1)\right) \varphi_{\sigma(i_2)}(x_2) \cdots \varphi_{\sigma(i_N)} +$$

$$\varphi_{\sigma(i_1)}(x_1) \left(h(r_2)\, \varphi_{\sigma(i_2)}(x_2)\right) \cdots \varphi_{\sigma(i_N)} +$$

$$\cdots\cdots$$

$$+ \varphi_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_{N-1})}(x_{N-1}) \left(h(\bar{r}_N)\varphi_{\sigma(i_N)}(x_N)\right) \Big\}$$

$$= \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\operatorname{sgn}\sigma} \left(\epsilon_{\sigma(i_1)} + \cdots + \epsilon_{\sigma(i_N)}\right) \varphi_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_N)}(x_N)$$

$$= \left(\epsilon_{i_1} + \cdots + \epsilon_{i_N}\right) \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\operatorname{sgn}\sigma} \varphi_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_N)}(x_N)$$

$$= \left(\epsilon_{i_1} + \cdots + \epsilon_{i_N}\right) \Psi_I = E_I \Psi_I$$

where we used that

$$\left(\epsilon_{\sigma(i_1)} + \cdots + \epsilon_{\sigma(i_N)}\right) = \epsilon_{i_1} + \cdots + \epsilon_{i_N}$$

for all permutations σ, and we defined

$$E_I = \epsilon_{i_1} + \cdots + \epsilon_{i_N} \qquad (7)$$

Let us now show that the Ψ_I for $I = (i_1, \ldots, i_N)$, $i_1 < \ldots < i_N$ form a complete orthonormal set, i.e.

$$\langle \Psi_I | \Psi_J \rangle = \delta_{IJ} = \delta_{i_1 j_1} \cdots \delta_{i_N j_N} \qquad (8)$$

where
$$I = (i_1, \ldots, i_N) \quad , \; i_1 < \ldots < i_N$$
$$J = (j_1, \ldots, j_N) \quad , \; j_1 < \ldots < j_N$$

The index ordering is necessary since interchanging indices gives a linearly dependent function; for example $\Psi_{i_1 i_2}(x_1, x_2) = -\Psi_{i_2 i_1}(x_1, x_2)$.

Let us show that (8) is true.

$$\langle \Psi_I | \Psi_J \rangle = \int dx_1 \ldots dx_N \, \Psi_I^*(x_1 \ldots x_N) \Psi_J(x_1 \ldots x_N)$$

$$= \int dx_1 \ldots dx_N \frac{1}{N!} \left(\sum_\sigma (-1)^{\operatorname{sgn} \sigma} \varphi^*_{\sigma(i_1)}(x_1) \cdots \varphi_{\sigma(i_N)}(x_N) \right)$$
$$\times \left(\sum_\pi (-1)^{\operatorname{sgn} \pi} \varphi_{\pi(j_1)}(x_1) \cdots \varphi_{\pi(j_N)}(x_N) \right)$$

where σ and π are permutations of N elements

This gives

$$\langle \Psi_I | \Psi_J \rangle = \frac{1}{N!} \sum_{\sigma, \pi} (-1)^{\operatorname{sgn} \sigma + \operatorname{sgn} \pi}$$
$$\times \left(\int dx_1 \, \varphi^*_{\sigma(i_1)}(x_1) \varphi_{\pi(j_1)}(x_1) \right) \cdots \cdots \left(\int dx_N \, \varphi^*_{\sigma(i_N)}(x_N) \varphi_{\pi(j_N)}(x_N) \right)$$

$$= \frac{1}{N!} \sum_{\sigma, \pi} (-1)^{\operatorname{sgn} \sigma + \operatorname{sgn} \pi} \delta_{\sigma(i_1) \pi(j_1)} \cdots \delta_{\sigma(i_N) \pi(j_N)} \qquad (9)$$

Now it is clear that if $\{i_1 .. i_N\}$ and $\{j_1 .. j_N\}$ are not the same sets of elements, then at least one of the Kronecker deltas vanishes, so

$$\langle \Psi_I | \Psi_J \rangle = 0 \quad \text{if} \quad I \neq J$$

On the other hand if $I = J$ then

$$\langle \Psi_I | \Psi_I \rangle = \frac{1}{N!} \sum_{\sigma,\pi} (-1)^{\operatorname{sgn}\sigma + \operatorname{sgn}\pi} \delta_{\sigma(i_1)\pi(i_1)} \cdots \delta_{\sigma(i_N)\pi(i_N)}$$

and this is only nonzero if $\sigma = \pi$, so

$$\langle \Psi_I | \Psi_I \rangle = \frac{1}{N!} \sum_{\sigma} \delta_{\sigma(i_1)\sigma(i_1)} \cdots \delta_{\sigma(i_N)\sigma(i_N)}$$

$$= \frac{1}{N!} \sum_{\sigma} 1 = \frac{1}{N!} \cdot N! = 1$$

which proves Eq. (8).

The fact that the Ψ_I form a complete set implies that any fermionic state Ψ can be expanded in them, i.e.

$$\Psi = \sum_{i_1 < \cdots < i_N} c_{i_1 \cdots i_N} \Psi_{i_1 \cdots i_N} \tag{10}$$

where $c_{i_1 \cdots i_N} = \langle \Psi_{i_1 \cdots i_N} | \Psi \rangle$

This is the basis of the configuration interaction (CI) - method commonly used in quantum chemistry.

Density matrices

The k-particle density matrix is defined as

$$\tilde{\Gamma}_k(x_1 \dots x_k; x_1' \dots x_k') = \frac{N!}{(N-k)!}\int dx_{k+1} \dots dx_N \, \Psi(x_1 \dots x_N) \Psi^*(x_1' \dots x_k', x_{k+1} \dots x_N) \quad (11)$$

and its diagonal $\tilde{\Gamma}_k(x_1 \dots x_k; x_1 \dots x_k)$ is given by

$$\Gamma_k(x_1 \dots x_k) = \frac{N!}{(N-k)!}\int dx_{k+1} \dots dx_N \, |\Psi(x_1 \dots x_N)|^2 \quad (12)$$

Our main interest is in Γ_2 but it turns out that it is useful to consider Γ_k as well for the case that $\Psi = \Psi_I$, a Slater determinant.

We start by calculating $\tilde{\Gamma}_1$ for $\Psi = \Psi_I$. Then

$$\tilde{\Gamma}_1(x_1; x_1') = \frac{N!}{(N-1)!}\int dx_2 \dots dx_N \, \Psi_I(x_1 \dots x_N) \Psi_I^*(x_1', x_2 \dots x_N)$$

$$= N \cdot \frac{1}{N!}\sum_{\sigma,\pi}(-1)^{\operatorname{sgn}\sigma + \operatorname{sgn}\pi}\int dx_2 \dots dx_N \, \varphi_{\sigma(i_1)}(x_1) \dots \varphi_{\sigma(i_N)}(x_N)\, \varphi_{\pi(i_1)}(x_1')\varphi_{\pi(i_2)}(x_2) \dots \varphi_{\pi(i_N)}(x_N)$$

$$= \frac{1}{(N-1)!}\sum_{\sigma,\pi}(-1)^{\operatorname{sgn}\sigma + \operatorname{sgn}\pi} \varphi_{\sigma(i_1)}(x_1)\varphi^*_{\pi(i_1)}(x_1')\, \delta_{\sigma(i_2)\pi(i_2)} \dots \delta_{\sigma(i_N)\pi(i_N)}$$

This is zero unless σ and π map $(i_2 \dots i_N)$ to the same set, but then they must also map i_1 to the same index, i.e. we have zero unless $\sigma = \pi$. So

$$\tilde{\Gamma}_1(x_1; x_1') = \frac{1}{(N-1)!}\sum_{\sigma}\varphi_{\sigma(i_1)}(x_1)\varphi^*_{\sigma(i_1)}(x_1')$$

$$= \frac{1}{(N-1)!}(N-1)!\left(\varphi_{i_1}(x_1)\varphi^*_{i_1}(x_1') + \dots + \varphi_{i_N}(x_1)\varphi^*_{i_N}(x_1')\right)$$

$\Rightarrow$

$$\tilde{\Gamma}_1(x_1;x_1') = \varphi_{i_1}(x_1)\varphi_{i_1}^*(x_1') + \dots + \varphi_{i_N}(x_1)\varphi_{i_N}^*(x_1')$$

where we used that there are always $(N-1)!$ permutations that map i_1 to a given index.

We often use the notation

$$\gamma(x_1,x_1') = \tilde{\Gamma}_1(x_1;x_1')$$

So

$$\gamma(x_1,x_1') = \sum_{k=1}^{N} \varphi_{i_k}(x_1)\varphi_{i_k}^*(x_1') \qquad (13)$$

Let us now demonstrate that γ (for noninteracting systems) has the following property called idempotency.

$$\gamma(x_1,x_1') = \int dy\, \gamma(x_1,y)\gamma(y,x_1') \qquad (14)$$

Proof: $\int dy\, \gamma(x_1,y)\gamma(y,x_1')$

$$= \int dy \sum_{k=1}^{N} \varphi_{i_k}(x_1)\varphi_{i_k}^*(y) \sum_{l=1}^{N} \varphi_{i_l}(y)\varphi_{i_l}^*(x_1')$$

$$= \sum_{k,l=1}^{N} \varphi_{i_k}(x_1)\varphi_{i_l}^*(x_1')\,\delta_{i_k i_l} = \sum_{k=1}^{N} \varphi_{i_k}(x_1)\varphi_{i_k}^*(x_1')$$

$$= \gamma(x_1,x_1')$$

which proves the statement.

Let us now calculate $\Gamma_k(x_1 \ldots x_k)$ for a non-interacting system, i.e. for $\Psi = \Psi_I$ in Eq. (12).

Theorem: If $\Psi = \Psi_I$ then

$$\Gamma_k(x_1 \ldots x_k) = \begin{vmatrix} \gamma(x_1,x_1) & \cdots & \gamma(x_1,x_k) \\ \vdots & & \vdots \\ \gamma(x_k,x_1) & \cdots & \gamma(x_k,x_k) \end{vmatrix} \qquad (15)$$

with γ given by Eq. (13).

To prove Eq. (15) we use induction:

1) We show that (15) is true for $k=N$
2) We prove that if (15) is true for k then it is also true for $k-1$.

Before giving the proof we derive the following property valid for general Γ_k: (from Eq. (12))

$$\int dx_k\, \Gamma(x_1, \ldots, x_k) = \frac{N!}{(N-k)!} \int dx_k\, dx_{k+1} \cdots dx_N\, |\Psi(x_1 \ldots x_N)|^2$$

$$= \frac{N!}{(N-k)!} \frac{(N-(k-1))!}{N!} \Gamma_{k-1}(x_1 \ldots x_{k-1})$$

$$= (N-k+1)\, \Gamma_{k-1}(x_1 \ldots x_{k-1})$$

So:

$$\Gamma_{k-1}(x_1 \ldots x_{k-1}) = \frac{1}{(N-k+1)} \int dx_k\, \Gamma_k(x_1, \ldots, x_k) \qquad (16)$$

Let us now first prove that (15) is true for $N=k$.
We use the following property of determinants

$$\det A = \det A^T \qquad \det(AB) = \det(A)\cdot\det(B)$$

for matrices A and B, where A^T is the transpose of A.
We have for $\Psi = \Psi_I$ and $k=N$

$$\Gamma_N(x_1 \dots x_N) = \frac{N!}{0!}\,|\Psi_I(x_1 \dots x_N)|^2$$

$$= \frac{N!}{N!}\begin{vmatrix} \varphi_{i_1}(x_1) & \cdots & \varphi_{i_N}(x_1) \\ \vdots & & \vdots \\ \varphi_{i_1}(x_N) & \cdots & \varphi_{i_N}(x_N)\end{vmatrix} \cdot \overbrace{\begin{vmatrix} \varphi^*_{i_1}(x_1) & \cdots & \varphi^*_{i_N}(x_1) \\ \vdots & & \vdots \\ \varphi^*_{i_1}(x_N) & \cdots & \varphi^*_{i_N}(x_N)\end{vmatrix}}^{A}$$

$$= \frac{N!}{N!}\left|\begin{pmatrix} \varphi_{i_1}(x_1) & \cdots & \varphi_{i_N}(x_1) \\ \vdots & & \vdots \\ \varphi_{i_1}(x_N) & \cdots & \varphi_{i_N}(x_N)\end{pmatrix} \underbrace{\begin{pmatrix} \varphi^*_{i_1}(x_1) & \cdots & \varphi^*_{i_1}(x_N) \\ \vdots & & \vdots \\ \varphi^*_{i_N}(x_1) & \cdots & \varphi^*_{i_N}(x_N)\end{pmatrix}}_{A^T}\right|$$

$$= 1\cdot\begin{vmatrix} \gamma(x_1,x_1) & \cdots & \gamma(x_1,x_N) \\ \vdots & & \vdots \\ \gamma(x_N,x_1) & \cdots & \gamma(x_N,x_N)\end{vmatrix}$$

which proves what we wanted.

Now we will prove the induction step mentioned on p. 7.

Suppose (15) is valid for k, then for $k-1$ we have according to Eq. (16)

$$\Gamma_{k-1}(x_1 \cdots x_N) = \frac{1}{(N-k+1)} \int dx_k \begin{vmatrix} \gamma(x_1,x_1) & \cdots & \gamma(x_1,x_k) \\ \vdots & & \vdots \\ \gamma(x_k,x_1) & \cdots & \gamma(x_k,x_k) \end{vmatrix} \quad (17)$$

We expand Eq. (17) along column k, i.e.

$$\Gamma_{k-1}(x_1 \cdots x_N) = \frac{1}{(N-k+1)} \int dx_k \sum_{j=1}^{k} (-1)^{k+j} \gamma(x_j,x_k) D_{jk} \quad (18)$$

where D_{jk} is the subdeterminant of (15) with row j and column k removed, i.e.

$$D_{jk} = \begin{vmatrix} \gamma_{11} & \cdots & \gamma_{1k-1} \\ \vdots & & \vdots \\ \gamma_{k1} & \cdots & \gamma_{kk-1} \end{vmatrix} \; j \leftarrow \text{removed}$$

k removed

and we use the compact notation $\gamma_{jk} = \gamma(x_j, x_k)$

We can then take out $j=k$ separately and write for (18)

$$\Gamma_{k-1} = \frac{1}{(N-k+1)} \int dx_k \left[\gamma(x_k,x_k) D_{kk} + \sum_{j=1}^{k-1} (-1)^{j+k} \gamma(x_j,x_k) D_{jk} \right] \quad (19)$$

Now $\int dx_k\, \gamma(x_k,x_k) = \int dx_k\, n(x_k) = N$ so that (19) becomes

$$\Gamma_{k-1} = \frac{1}{(N-k+1)} \left[N D_{kk} + \sum_{j=1}^{k-1} (-1)^{j+k} \int dx_k\, \gamma(x_j,x_k) D_{jk} \right] \quad (20)$$

Let us now look at the last term in (20)

$$\int dx_k\, \gamma(x_j,x_k)\, D_{jk} = \int dx_k\, \gamma(x_j,x_k) \begin{array}{c} \left| \begin{array}{ccc} \gamma_{11} & \cdots & \gamma_{1k-1} \\ \vdots & & \vdots \\ - & - & - \\ \vdots & & \vdots \\ \gamma_{k1} & \cdots & \gamma_{kk-1} \end{array} \right| \begin{array}{c} \\ \\ j \\ \\ \\ \end{array} \\ k \end{array}$$

$$= \begin{array}{c} \left| \begin{array}{cccc} \gamma_{11} & - & - & \gamma_{1k-1} \\ \vdots & & & \vdots \\ - & - & - & - \\ \vdots & & & \vdots \\ \int dx_k\, \gamma_{jk}\gamma_{k1} & \int dx_k\, \gamma_{jk}\gamma_{k2} & \cdots & \int dx_k\, \gamma_{jk}\gamma_{kk-1} \end{array} \right| \begin{array}{c} \\ \\ j \\ \\ \\ \end{array} \\ k \end{array}$$

where we inserted the x_k integration into the last row of the determinant since integration is a linear operation.

Using the idempotency property (14) we then have

$$\int dx_k\, \gamma(x_j,x_k)\, D_{jk} = \begin{array}{c} \left| \begin{array}{ccc} \gamma_{11} & \cdots & \gamma_{1k-1} \\ \vdots & & \vdots \\ - & - & - \\ \vdots & & \vdots \\ \gamma_{k-1\,1} & \cdots & \gamma_{k-1,k-1} \\ \gamma_{j1} & \cdots & \gamma_{jk-1} \end{array} \right| \begin{array}{c} \\ \\ j \\ \\ \\ \\ \end{array} \\ k \end{array}$$

so we in some sense reconstructed row j but it is moved to row $k-1$. It requires $(k-1)-j$ $= k-j-1$ row swaps to move it back to row j, so that using that every swap induces a $-$ sign:

$$\int dx_k\, \gamma(x_j,x_k)\, D_{jk} = (-1)^{k-j-1} \left| \begin{array}{ccc} \gamma_{11} & \cdots & \gamma_{1k-1} \\ \vdots & & \vdots \\ \gamma_{k-1,1} & \cdots & \gamma_{k-1\,k-1} \end{array} \right|$$

$$= (-1)^{k-j-1} D_{kk} \qquad (21)$$

Putting this result back in (20) then gives

$$\Gamma_{k-1} = \frac{1}{(N-k+1)} \left[N D_{kk} + \sum_{j=1}^{k-1} (-1)^{j+k} \cdot (-1)^{j-k-1} D_{kk} \right]$$

$$= \frac{1}{(N-k+1)} \left[N D_{kk} - \sum_{j=1}^{k-1} D_{kk} \right] = \frac{N D_{kk} - (k-1) D_{kk}}{N-k+1}$$

$$= D_{kk} = \begin{vmatrix} \gamma(x_1, x_1) & \cdots & \gamma(x_1, x_{k-1}) \\ \vdots & & \vdots \\ \gamma(x_{k-1}, x_1) & \cdots & \gamma(x_{k-1}, x_{k-1}) \end{vmatrix} .$$

which proves the induction step.

By this Eq. (15) is proven for all $k \in \{1, \ldots, N\}$.

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Using Eq. (15) we can calculate $\Gamma_2(x_1, x_2)$ for a non-interacting Ψ_I. We obtain

$$\Gamma_2(x_1, x_2) = \begin{vmatrix} \gamma(x_1, x_1) & \gamma(x_1, x_2) \\ \gamma(x_2, x_1) & \gamma(x_2, x_2) \end{vmatrix} \qquad (22)$$

$$= \gamma(x_1, x_1)\gamma(x_2, x_2) - \gamma(x_1, x_2)\gamma(x_2, x_1)$$

$$= n(x_1) n(x_2) - |\gamma(x_1, x_2)|^2$$

where we used $\left\{ \begin{array}{l} n(x_1) = \gamma(x_1, x_1) \\ \gamma(x_1, x_2)^* = \gamma(x_2, x_1) \end{array} \right.$

Eq. (22) can be used to calculate the interaction energy for a non-interacting state.

If

$$\hat{W} = \frac{1}{2}\sum_{i\neq j}^{N} w(\bar{r}_i, \bar{r}_j)$$

Then

$$\langle \Psi | \hat{W} | \Psi \rangle = \frac{1}{2}\int dx_1 dx_2 \, \Gamma_2(x_1, x_2)\, w(\bar{r}_1, \bar{r}_2)$$

So using Eq. (22) we have

$$\langle \Psi_I | \hat{W} | \Psi_I \rangle = \frac{1}{2}\int dx_1 dx_2 \, n(x_1) n(x_2)\, w(\bar{r}_1, \bar{r}_2) \quad (= E_H)$$

$$- \frac{1}{2}\int dx_1 dx_2 \, |\gamma(x_1, x_2)|^2 w(r_1, r_2) \quad (= E_x)$$

$$= E_H[n] + E_x[n]$$

which define the Hartree and exchange energy for the case that Ψ_I is the ground state Kohn-Sham wavefunction.

Since we defined $E_{Hxc}[n]$ before we can define the correlation energy as

$$E_c[n] = E_{Hxc}[n] - E_H[n] - E_x[n]$$

and write

$$E = T_s[n] + \int dx \, n(x) v(\bar{r}) + E_H[n] + E_x[n] + E_c[n]$$