

## Higher eigenvalues and eigenfunctions, the Exclusion Principle

Consider again the quadratic form  $E_\psi$  under the same assumptions as in the previous section, i.e., that  $V \in L^{n/2}(R^n) + L^\infty(R^n)$  and  $V$  vanish at infinity in measure. The existence of a ground state has been established in the previous section, i.e., we know that there is a function  $\psi_0 \in H^1(R^n)$  such that

$$E_{\psi_0} = E_0$$

where

$$E_0 = \inf\{E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1\} .$$

Also note that for any  $f \in H^1(R^n)$

$$F(\varepsilon) := \frac{E_{\psi_0 + \varepsilon f}}{\|\psi_0 + \varepsilon f\|^2} \geq \frac{E_{\psi_0}}{\|\psi_0\|^2} = E_0$$

and hence  $F'(0) = 0$  which reads as

$$\int \nabla \psi_0 \cdot \nabla f dx + \int V(x) \psi_0(x) f(x) dx = E_0 \int \psi_0(x) f(x) dx .$$

In the language of partial differential equations one says that  $\psi_0$  is a weak solution of the eigenvalue problem

$$-\Delta \psi_0(x) + V(x) \psi_0(x) = E_0 \psi_0(x) .$$

Likewise we can find the next higher eigenfunction as follows. Consider the minimization problem

$$E_1 = \inf\{E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1, (\psi, \psi_0) = 0\} .$$

As in the previous section we see that a minimizer exists for this problem under the condition that  $E_1 < 0$ . The only new thing to check is that the for the minimizing sequence, call it  $\phi_j$  with  $\phi_j \rightharpoonup \psi_1$ ,

$$\lim_{j \rightarrow \infty} (\phi_j, \phi_0) = (\psi_1, \psi_0) = 0$$

which follows immediately from the definition of weak convergence. Consider again a function

$$F(\varepsilon) := \frac{E_{\psi_1 + \varepsilon f}}{\|\psi_1 + \varepsilon f\|^2}$$

where  $f \in H^1(R^n)$  such that  $(f, \psi_0) = 0$ . Since  $F(\varepsilon) \geq E_1 = F(0)$  we by differentiating that

$$L_1(f) := \int \nabla \psi_1 \cdot \nabla f dx + \int V(x) \psi_1(x) f(x) dx = E_0 \int \psi_1(x) f(x) dx ,$$

for all  $f \in H^1(R^n)$  with  $(f, \psi_0) = 0$ . From that it follows that there exists a constant  $\mu$  so that  $L_1(f) - E_0(\psi_1, f) = \mu(\psi_0, f)$  for all  $f \in H^1(R^n)$ . In particular choosing  $f = \psi_0$  we get

$$\int \nabla \psi_1 \cdot \nabla \psi_0 dx + \int V(x) \psi_1(x) \psi_0(x) dx = \mu \|\psi_0\|^2$$

while at the same time

$$\int \nabla \psi_1 \cdot \nabla \psi_0 dx + \int V(x) \psi_1(x) \psi_0(x) dx = E_0(\psi_1, \psi_0) = 0 .$$

Hence  $\mu = 0$ . Therefore, we conclude that

$$\int \nabla \psi_1 \cdot \nabla f dx + \int V(x) \psi_1(x) f(x) dx = E_0 \int \psi_1(x) f(x) dx$$

for all  $f \in H^1(R^n)$ . Hence  $\psi_1$  is a weak solution of the eigenvalue equation

$$-\Delta \psi_1(x) + V(x) \psi_1(x) = E_1 \psi_1(x) .$$

We have, tacitly, assumed that the functions  $\psi_0$  and  $\psi_1$  are real. Please show that they can be chosen to be real.

In a similar fashion we can now define the other higher eigenvalues and eigenfunctions recursively by minimizing

$$E_k = \inf \{ E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1, (\psi, \psi_l) = 0, l = 0, 1, \dots, k-1 \} .$$

As before we find that  $L_k(f) = E_k(\psi_k, f)$  for all  $f \in H^1(R^n)$  with  $(f, \psi_l) = 0, l = 0, 1, \dots, k-1$ . Again from this it follows that  $L_k(f) = \sum_{l=0}^{k-1} \mu_k(f, \psi_l)$  for all  $f \in H^1(R^n)$  for some numbers  $\mu_0, \mu_1, \dots, \mu_{k-1}$ . Assuming inductively that  $L_l(f) = E_l(\psi_l, f)$  for all  $f \in H^1(R^n)$  we get that on the one hand  $L_k(\psi_m) = \mu_m \|\psi_m\|_2^2$ , while on the other  $L_k(\psi_m) = L_m(\psi_k) = E_k(\psi_m, \psi_k) = 0$ . Hence  $\mu_l = 0, l = 0, \dots, k-1$ .

Continuing this way we get a sequence of negative numbers  $E_k$  together with function  $\psi_k$ . About this sequence we can state the following theorem.

**Theorem: Higher eigenvalues and eigenfunctions** *The sequence  $E_k$  is either finite or infinite in which case it can only accumulate at 0. In particular the eigenvalues can only be finitely degenerate.*

PROOF: Assume that the sequence of eigenvalues  $E_k$  is not finite. We may also assume that the eigenfunctions are normalized to one and are orthogonal to each other. We have to show that the sequence  $E_k$  converges to zero. Suppose not, i.e., there exists a number  $-A$  so that infinitely many eigenvalues are below that number. This means that

$$E_{\psi_k} = E_k \|\psi_k\|^2 < -A \|\psi_k\|^2 . \tag{1}$$

and since the energy dominates the kinetic energy we get

$$\|\nabla \psi_k\|^2 \leq 2E_{\psi_k} + \Lambda \|\psi_k\|_2^2 \leq (\Lambda - A) .$$

In other words, the sequence  $\psi_k$  is a bounded sequence in  $H^1(R^n)$ . Since the sequence is orthonormal it converges weakly to zero. Pick  $A > \varepsilon > 0$  and recall that

$$\left| \int V(x) |\psi_k(x)|^2 dx \right| \leq \left| \int_{N > |V| > \varepsilon} V(x) |\psi_k(x)|^2 dx \right| +$$

$$\begin{aligned}
& + \left| \int_{|V| \geq N} V(x) |\psi_k(x)|^2 dx \right| + \left| \int_{|V| \leq \varepsilon} V(x) |\psi_k(x)|^2 dx \right| \\
& \leq N \left| \int_{N > |V| > \varepsilon} |\psi_k(x)|^2 dx \right| + \left( \int_{|V| \geq N} |V(x)|^{n/2} dx \right)^{2/n} \|\psi_k\|_{2n/(n-2)}^2 + \varepsilon \|\psi_k\|_2^2 .
\end{aligned}$$

By the Sobolev inequality the second factor in the second term is uniformly bounded. Fix  $N$  large enough can make the second term less than  $\varepsilon$  uniformly in  $k$ . Since  $\{x : |V(x)| > \varepsilon\}$  has finite measure we learn from the Rellich Kondrachev Theorem that the first term tends to zero as  $k \rightarrow \infty$ . Hence

$$\limsup_{k \rightarrow \infty} \left| \int V(x) |\psi_k(x)|^2 dx \right| < 2\varepsilon$$

and hence

$$\lim_{k \rightarrow \infty} \left| \int V(x) |\psi_k(x)|^2 dx \right| = 0 . \quad (2)$$

But this contradicts equation (1).

In quantum mechanics, the state of many particles is described a wave function on the configuration space of these particles. More precisely given  $N$  particles with coordinates  $x_1, \dots, x_N$  then the wave function

$$\Psi(x_1, \dots, x_N)$$

is a function in  $L^2(\mathbb{R}^{3N})$  and its interpretation is that

$$|\Psi(x_1, \dots, x_N)|^2$$

is the probability density of finding the first particle at  $x_1$  the second particle at  $x_2$  etc.

It is a fundamental law that wave functions of identical elementary particles come in two flavors.

FERMIONS: The wave function

$$\Psi(x_1, \dots, x_N)$$

is antisymmetric under exchange of particle labels, i.e.,

$$\Psi(x_{\pi(1)}, \dots, x_{\pi(N)}) = (-)^\pi \Psi(x_1, \dots, x_N) ,$$

where  $\pi$  is any permutation of  $N$  objects and  $(-)^\pi$  is the signature of the permutation, that is  $-1$  for odd permutation and  $+1$  for even permutations.

BOSONS: The wave function

$$\Psi(x_1, \dots, x_N)$$

is symmetric under exchange of particle labels, that is

$$\Psi(x_{\pi(1)}, \dots, x_{\pi(N)}) = \Psi(x_1, \dots, x_N) ,$$

where  $\pi$  is any permutation of  $N$  objects.

If we have  $K$  bosons and  $N$  fermions then the wave function of the combined system is given by

$$\Psi(R_1, \dots, R_K, x_1, \dots, x_N)$$

where the function is symmetric under permutation of the first  $K$  labels and antisymmetric under permutations of the other  $N$  labels.

There is an added complication because of the spin but we neglect this possibility for the moment.

As in the one particle case we can now write down an energy for a system of  $N$  *non-interacting* particles

$$E_\Psi = T_\Psi + V_\Psi$$

where

$$T_\Psi = \sum_{j=1}^N \int_{R^{3N}} |\nabla_{x_j} \Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N ,$$

and

$$V_\Psi = \sum_{j=1}^N \int_{R^{3N}} V(x_j) |\Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N .$$

We shall make the same assumption about the potential as in the case of one particle.

The problem is now to find

$$E_0(N) = \inf \{ E_\Psi : \Psi \in H^1(R^{3N}), \|\Psi\|_{L^2(R^{3N})} = 1 \} .$$

**Theorem: Minimization for non interacting bosons** *The ground state energy for  $N$  noninteracting bosons is given by*

$$E_0(N) = N E_0$$

*and the corresponding minimizer is given by*

$$\prod_{j=1}^N \psi_0(x_j)$$

*where  $\psi_0$  is the normalized ground state wave function of the single particle problem.*

PROOF: Clearly by using  $\prod_{j=1}^N \psi_0(x_j)$  as a normalized trial function we see right away that  $E_0(N) \leq NE_0$ . To see the converse is a bit more difficult. Define the **one particle density associated with  $\Psi$**  by

$$\rho(x) = N \int_{R^{3(N-1)}} |\Psi(x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N .$$

Note it is immaterial over which variable we integrate since the function  $|\Psi(x_1, \dots, x_N)|^2$  is symmetric. this definition holds for bosonic wave functions as well as for fermionic wave functions. For our boson wave function we calculate

$$|\nabla \sqrt{\rho}(x)|^2 = N \left[ \frac{1}{\sqrt{\rho}(x)} \int_{R^{3(N-1)}} \Psi(x, x_2, \dots, x_N) \nabla_x \Psi(x, x_2, \dots, x_N) dx_2 \cdots dx_N \right]^2$$

and by Schwarz's inequality we obtain the bound

$$\begin{aligned} |\nabla \sqrt{\rho}(x)|^2 &\leq \left[ \frac{1}{\sqrt{\rho}(x)} N \sqrt{\rho(x)} \int |\nabla_x \Psi(x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N \right] \\ &= N \int |\nabla_x \Psi(x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N , \end{aligned}$$

and upon integrating over  $x$ , using the symmetry of the wave function we get the Hoffmann-Ostenhof inequality

$$\int_{R^3} |\nabla \sqrt{\rho}(x)|^2 dx \leq T_\Psi .$$

In particular we learn that  $\sqrt{\rho} \in H^1(R^3)$ . Note that a simple calculation reveals that

$$V_\Psi = \int_{R^3} V(x) \rho(x) dx .$$

Thus, we see that

$$E_\Psi \geq \int_{R^3} |\nabla \sqrt{\rho}(x)|^2 dx + \int_{R^3} V(x) \rho(x) dx$$

which we have to minimize over all  $\sqrt{\rho} \in H^1(R^3)$  with  $\int \rho = N$ . Put it differently, we can define  $\sqrt{N} \psi(x) = \sqrt{\rho}(x)$  and have to minimize the one particle problem  $NE_\psi$  over all  $\psi \in H^1(R^3)$  with  $\|\psi\| = 1$  which equals  $NE_0$ . Hence have that  $E_0(N) = E_0$  and  $\prod_{j=1}^N \psi_0(x_j)$  is a minimizer. If  $\Psi_0$  is any other minimizer there must be equality in all the above inequalities. In particular equality in Schwarz's inequality leads to

$$\lambda_j(x) \Psi(x, x_2, \dots, x_N) = \nabla_j \Psi(x, x_2, \dots, x_N)$$

for a.e.  $x_2, \dots, x_N$ . Because of the symmetry of the function under prmutation,  $\Psi$  must be a product function of the form  $\prod_{j=1}^N \phi(x_j)$  and insiring this function into the functional we get that

$$N[T_\phi + V_\phi] = NE_0$$

and hence  $\phi$  must be the ground state of the one body problem which, as we have argued somewhere else is unique.

**Theorem: Minimization for non interacting fermions** *The ground state energy for  $N$  noninteracting fermions is given by*

$$E_0(N) = \sum_{j=0, E_j \leq 0}^{N-1} E_j \quad (3)$$

and the corresponding minimizer is given by a **slater determinant**

$$\frac{1}{\sqrt{N!}} \det(\psi_i(x_j))$$

where  $\psi_i$  is the normalized eigenfunctions associated with the eigenvalues  $E_0, E-1, \dots, E_{N-1}$  of the single particle problem. If the number of non-positive eigenvalues is strictly less than  $N$  there is no minimizer but the energy is just the sum over the available non positive eigenvalues.

This Theorem is quite a bit trickier. Note that we can write

$$\begin{aligned} \sum_{i=1}^N \int |\nabla_{x_i} \Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N &= N \int |\nabla_{x_1} \Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N \\ &= \int [\nabla_x \nabla_y \rho](x, x) dx \end{aligned} \quad (4)$$

where the **one particle density matrix**  $\rho$  is given by

$$\rho_{\Psi}(x, y) = N \int \overline{\Psi(x, \dots, x_N)} \Psi(y, \dots, x_N) dx_2 \cdots dx_N .$$

Likewise,

$$\begin{aligned} \sum_{i=1}^N \int V(x_i) |\Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N &= N \int V(x_1) |\Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N \\ &= \int V(x) \rho_{\Psi}(x, x) dx . \end{aligned}$$

Note that

$$\rho_{\Psi}(y, x) = \overline{\rho_{\Psi}(x, y)}$$

and hence  $\rho(x, y)$  defines a selfadjoint operator. Denote its eigenfunctions by  $\phi_j(x)$  which we can choose to be orthonormal, i.e.,

$$(\phi_i, \phi_j) = \delta_{i,j} .$$

We denote its eigenvalues by  $\lambda_j$ . The following Lemma (which I learned from Elliott Lieb) is important.

**Lemma** *The operator defined by the kernel  $\rho_\Psi(x, y)$  has non-negative eigenvalues and is trace class, in particular*

$$\sum_j \lambda_j = N .$$

Moreover, we have the surprising fact that all the eigenvalues are less than 1.

PROOF: It is a standard fact that the kernel has an complete set of orthonormal eigenfunctions  $\phi_j$ , and we can write

$$\rho_\Psi(x, y) = \sum_{j=1}^{\infty} \lambda_j \overline{\phi_j(x)} \phi_j(y) .$$

The trace of the associated operator is defined by integrating

$$\int \sum_{j=1}^{\infty} \lambda_j |\phi_j(x)|^2 dx = N \int |\Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N = N .$$

To see that the eigenvalues are less than one we have to use the antisymmetry of  $\Psi$ . It suffice to show that for any  $f \in L^2(R^n)$  we have that

$$\int \overline{f(x)} \rho_\Psi(x, y) f(y) dx dy \leq \|f\|_2^2 .$$

Consider now the integral kernel

$$K(x_1, \dots, x_N, y_1, \dots, y_N) = \sum_{j=1}^N \overline{f(x_j)} f(y_j)$$

It is a sum of rank one projections. To describe the eigenfunctions we complement  $f$  to an orthonormal basis and denote it by  $f_j$ . The eigenfunctions of  $K$  are now all products of the form

$$f_{j_1}(x_1) \cdots f_{j_N}(x_N) .$$

(Note that we use here the spectral theorem of the operator  $K$  which is elementary in this case). The function  $\Psi$  can be expanded in terms of products of  $f_j$

$$\Psi(x_1, \dots, x_N) = \sum_{j_1, \dots, j_N} C(j_1, \dots, j_N) f_{j_1}(x_1) \cdots f_{j_N}(x_N) .$$

Since  $\Psi$  is antisymmetric, the coefficients  $C$  are antisymmetric in their variables. This means that  $C$  vanishes if any two indices are the same. Moreover, since  $\Psi$  is normalized we have that

$$\sum_{j_1, \dots, j_N} |C(j_1, \dots, j_N)|^2 = 1 .$$

Now we compute for  $j_1, \dots, j_N$  different indices

$$\left(\prod_k f_{j_k}, K \prod_k f_{j_k}\right) = \sum_{k=1}^N |(f, f_{j_k})|^2$$

and since all the indices are different, at most one term is not zero. Hence

$$\left(\prod_k f_{j_k}, K \prod_k f_{j_k}\right) \leq 1$$

and

$$(\Psi, K\Psi) \leq \sum_{j_1, \dots, j_N} |C(j_1, \dots, j_N)|^2 = 1 .$$

But

$$(\Psi, K\Psi) = N(f, \rho_\Psi f) ,$$

and this proves the lemma.

Now we return to (4) and note that

$$\int [\nabla_x \nabla_y \rho](x, x) dx = \sum_{j=1}^N \lambda_j \int |\nabla \psi_j(x)|^2 dx$$

and hence

$$E_\Psi = \sum_{j=1}^N \lambda_j \left[ \int |\nabla \psi_j(x)|^2 dx + \int V(x) |\phi_j(x)|^2 dx \right]$$

and since the functions are all orthonormal we get that

$$E_0(N) \geq \sum_{j=1}^N \lambda_j E_j . \tag{5}$$

The  $E_j$  are negative and all the  $0 \leq \lambda_j \leq 1$  and, moreover,  $\sum_j \lambda_j = N$ . Thus, we have to minimize over all values of  $\lambda_j$  satisfying the above two constraints. The solution of that minimization problem is achieved by choosing  $\lambda_j = 1, j = 1, \dots, N$  and  $\lambda_j = 0, j > N$ . This is nothing but the bathtub principle (see ‘Analysis’ on p. 28). In this case

$$E_0(N) \geq \sum_{j=1, E_j \leq 0}^N E_j .$$

The converse follows from a direct computation using the the slater determinant.

Note that the previous theorem is a precise version of what we mean by filling the energy levels.

Another important result concerning higher eigenfunctions is the min-max principle which we discuss next.

**Theorem; Min- Max principle** *Let  $\phi_0, \dots, \phi_{k-1}$  be any  $k$  orthonormal functions in  $H^1(\mathbb{R}^n)$ . Consider the matrix*

$$h_{i,j} = \int \nabla \phi_i \cdot \nabla \phi_j dx + \int V(x) \phi_i \phi_j .$$

*denote by  $\lambda_j, j = 0, \dots, k-1$  the eigenvalues ordered increasingly of the matrix  $H = (h_{i,j})$ . Then we have that*

$$E_j \leq \lambda_j , j = 0, \dots k - 1 .$$

PROOF: Denote by  $\vec{c}_j$  the eigenvectors of the matrix  $H$ . Clearly  $\chi_0 = \sum_i c_0^i \phi_i$  satisfies  $(\chi_0, \chi_0) = 1$  and

$$E_0 \leq \int |\nabla \chi_0|^2 dx + \int V(x) |\chi_0(x)|^2 dx = \lambda_0 .$$

Now we proceed by induction and assume that

$$E_j \leq \lambda_j , j = 0, \dots k - 2 .$$

The space spanned by the linear combinations of  $\phi_0, \dots, \phi_{k-1}$  is  $k$ -dimensional and hence there exists  $\chi = \sum d^i \phi_i$ , with  $(\chi, \chi) = 1$  such that

$$(\chi, \psi_i) = 0 , i = 0, 1, \dots k - 2 .$$

Hence, by the definition of  $E_{k-1}$  we have that

$$E_{k-1} \leq \int |\nabla \chi|^2 dx + \int V(x) |\chi(x)|^2 dx = (\vec{d}, H \vec{d}) \leq \lambda_{k-1} ,$$

since  $\lambda_{k-1}$  is the largest eigenvalue. This proves the theorem.

This theorem allows us to compare eigenvalues of various operators. E.g., assume that  $W(x)$  is another potential satisfying the same assumptions as  $V$  but with  $V(x) \leq W(x)$  for a.e.  $x$ . Denote by  $\mu_j$  the eigenvalues associated with the quadratic form

$$\int |\nabla \psi|^2 dx + \int W(x) |\psi|^2 dx .$$

Then

$$\lambda_j \leq \mu_j$$

for all  $j$ . Note that there maybe fewer eigenvalues for the  $W$  problem then for the  $V$  problem but in this case  $\mu_j = 0$  for  $j$  sufficiently large. The proof follows immediately from the min-max principle.