It will be quickly seen that \( \inf_{\gamma \to q} \text{Tr}\{\gamma \hat{V}_{ee}\} \) must be extremely complicated, and to say it is "non-local" is an understatement.\(^1\)

— Elliot Lieb\(^{[43]}\)

3.1 **STRONGLY INTERACTING LIMIT IN DENSITY FUNCTIONAL THEORY**

In this chapter we will focus on the Strongly Interacting Limit of eq. (2.37), i.e.

\[
\lim_{\lambda \to \infty} F_{\lambda}[q] = \lim_{\lambda \to \infty} \left( T^\lambda[q] + \lambda V_{ee}^\lambda[q] \right). \tag{3.1}
\]

As shown later in sec. 3.3, arguments based on semi-classical analysis\(^{[14, 44]}\) seem to suggest that \( T^\lambda[q] \sim O(\sqrt{\lambda}) \) for \( \lambda \gg 1 \), implying that it can be neglected in the limit \( \lambda \to \infty \). We therefore define the Strongly Interacting Limit functional:

\[
V_{ee}^{\text{SIL}}[q] := \inf_{\Psi \to q} \langle \Psi | \hat{V}_{ee} | \Psi \rangle = \lim_{\lambda \to \infty} \frac{F_{\lambda}[q]}{\lambda}. \tag{3.2}
\]

Notice that we wrote eq. (3.2) as an infimum rather than a minimum, since the minimizer will turn out to be a distribution rather than a proper function: we recall that for every fixed \( \lambda \) the minimizer of \( F^\lambda[q] \) must be an eigenstate of the Hamiltonian \( \hat{H}^\lambda[q] \), eq. (2.39).

In \( \hat{H}^\lambda[q] \), the one-body potential \( \hat{V}^\lambda[q] \) is supposed to fix the density at all \( \lambda \), counterbalancing the effects of the operators \( \hat{T} \) and \( \hat{V}_{ee} \).

However, since we believe that the expectation value of the kinetic energy grows only as \( \sqrt{\lambda} \), in the limit \( \lambda \to \infty \) we must have

\[
\hat{V}^\lambda[q] = \lambda \sum_{i=1}^{N} \hat{V}^{\text{SIL}}[q](\mathbf{r}_i) + o(\lambda), \tag{3.3}
\]

in order to counter the infinite repulsion of the electron-electron operator. We therefore end up minimizing a classical operator:

\[
\min_{\Psi \to q} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^\lambda | \Psi \rangle = \lambda \inf_{\Psi \to q} \int \left( \hat{V}_{ee} + \hat{V}^{\text{SIL}} \right) | \Psi |^2. \tag{3.4}
\]

\(^1\) \( \overline{I}(q) = \inf\{\langle \Gamma | \Gamma \to q \rangle \} \) in the original text.
We see that the infimum in eq. (3.4) is achieved for a distribution $|Ψ_{\text{SIL}}(r_1, \ldots, r_N)|^2$ which is 0 everywhere except for the subspace $Ω_0$ in which

$$E_{\text{pot}}^{\text{SIL}}(r_1, \ldots, r_N) := \hat{V}_{ee} + \hat{V}^{\text{SIL}}$$

(3.5)

is minimum. Typically, the minimum of a manifold is a discrete set of points $\{s_1, \ldots, s_N\}$. This, however, would be inconsistent with a smooth density, which cannot be obtained if $|Ψ|^2 \approx \sum_1^N \delta(r_i - s_i)$. Imposing the constraint $Ψ \rightarrow ρ$ requires $Ω_0$ to be degenerate on a subspace of $ℝ^{dN}$ of dimension no less than $d$. If $d$ is indeed the dimension of $Ω_0$ we can write

$$Ω_0(s_1) = \{s_1, s_2 = \tilde{f}_2(s_1), s_3 = \tilde{f}_3(s_1), \ldots, s_N = \tilde{f}_N(s_1)\}, \quad s_1 \in \mathcal{P} \subseteq ℝ^d.$$

(3.6)

This is consistent with a deterministic solution to eq. (3.4) (see sec. 3.2 for further details), and it is what became known in the Chemistry community as Strictly Correlated Electrons, or SCE\(^2\).

In fact, eq. (3.6) is coherent with a physical picture in which, being the kinetic energy suppressed, the electron-electron interaction fixes the equilibrium position of the particles. The deterministic maps, or co-motion functions $\tilde{f}_i$ satisfy therefore

$$ρ(\tilde{f}_i(r)) \ d\tilde{f}_i(r) = ρ(r)dr, \quad i \in [1, \ldots, N] \subset \mathbb{N},$$

(3.7)

and can be imposed to satisfy the group properties\([16, 50]\):

$$\begin{align*}
\tilde{f}_1(r) &\equiv r, \\
\tilde{f}_2(r) &\equiv \tilde{f}(r), \\
\tilde{f}_3(r) &\equiv \tilde{f}(\tilde{f}(r)), \\
\vdots \\
\tilde{f}_N(r) &\equiv \tilde{f}(\underbrace{\tilde{f}(\ldots \tilde{f}(r) \ldots)}_{N-1 \text{ times}}) \\
&\equiv \underbrace{\tilde{f}(\tilde{f}(\ldots \tilde{f}(r) \ldots))}_{N \text{ times}} = r
\end{align*}$$

(3.8)

From eq. (3.7) we can read the physical meaning of the co-motion functions: since the number of particles in a volume $dr$ must be the same in each of the volumes $d\tilde{f}_i(r)$, the role of the co-motion functions is to provide the position of $N - 1$ electrons in terms of a reference electron.

Finally, the group properties (3.8) represented in fig. 3.1 are convenient, because they guarantee that the particles are indistinguishable.

\(^2\)It is worth noticing that the problem (3.4) does not always have a deterministic solution\([45, 46]\). Indeed, it is known that the minimizer of $E_{\text{pot}}^{\text{SIL}}$ is deterministic only in $d = 1$ or $N = 2$\([47–49]\).
3.1 Strongly Interacting Limit in Density Functional Theory

The minimizing SCE distribution then reads as a sum of configurations degenerate in energy which provides the correct density by means of eq. (2.5):

$$|\Psi_{\text{SCE}}|^2 = \frac{1}{N!} \sum_i \int \prod_{i=1}^{N} \frac{\rho(s)}{N} \delta(\mathbf{r}_i - \tilde{\mathbf{f}}_{\nu(i)}(s)) \, ds. \quad (3.9)$$

Using eq. (3.9) we can write an explicit form for the SCE functional:

$$V_{\text{SCE}}^\text{ee} = \int_{\mathbb{R}^{3N}} \hat{V}_{\text{ee}} |\Psi_{\text{SCE}}|^2$$

$$= \frac{1}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \int_{\mathbb{R}^{3}} \rho(\mathbf{r}) \nu_{\text{ee}}(|\tilde{\mathbf{f}}_i(\mathbf{r}) - \tilde{\mathbf{f}}_j(\mathbf{r})|) \, d\mathbf{r}$$

$$= \frac{1}{2} \sum_{i=1}^{N-1} \int_{\mathbb{R}^{3}} \rho(\mathbf{r}) \nu_{\text{ee}}(|\mathbf{r} - \tilde{\mathbf{f}}_i(\mathbf{r})|) \, d\mathbf{r}. \quad (3.10)$$

The associate multiplicative potential $v_{\text{SCE}}^{\text{ee}}(\mathbf{r})$ can be obtained in principle by applying eq. (2.40), i.e.:

$$\frac{\delta V_{\text{SCE}}^\text{ee}}{\delta \hat{\rho}(\mathbf{r})} \bigg|_{\hat{\rho} = \rho} = -v_{\text{SCE}}^{\text{ee}}(\mathbf{r}). \quad (3.11)$$

Being the comotion functions functionals of the density as well, via eq. (3.7), this computation is not the simplest. Luckily, the physical meaning of $\mathbf{f}_i$ provides us with a powerful shortcut to compute the effective external potential $v_{\text{SCE}}^{\text{ee}}$.

In fact, in the SCE regime the net force experienced by an electron in position $\mathbf{r}$ is given by $N - 1$ electrons located at position $\mathbf{f}_i(\mathbf{r})$. 

![Schematic representation of the group properties. Each arrow represents the application of the first non-trivial comotion function, $\tilde{\mathbf{f}}_2(s)$.](image_url)
This implies though that the force experienced by each particle is a function of the position of the particle itself. Imposing this force to be 0 at equilibrium implies that \( \forall i \)

\[
\nabla_i E_{\text{pot}}^{\SCE}(\mathbf{r}_1, \ldots, \mathbf{r}_N)|_{\Omega_0} = \nabla_i \left[ \frac{1}{2} \sum_{i \neq j}^N \psi_{\text{ee}}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^N \psi^{\SCE}[\mathbf{r}_i] \right] |_{\Omega_0} = 0, 
\]

or

\[
- \nabla \psi^{\SCE}[\mathbf{r}] = \sum_{i=2}^N \left[ \nabla \psi_{\text{ee}}(|\mathbf{r} - \mathbf{s}|) \right]_{\mathbf{s} = \tilde{\mathbf{f}}(\mathbf{r})}.
\]

### 3.1.0.1 The Seidl conjecture

In 1999, Seidl proposed\cite{7} an explicit construction scheme for the comotion functions \( \tilde{\mathbf{f}}_i \) based on integrals of the density for the \( d = 1 \) cases. Later in 2007, Seidl Gori Giorgi and Savin (SGS)\cite{50} generalized this construction to the spherically symmetric case in \( d = 3 \).

The Seidl conjecture has been proved, in the case of \( d = 1 \) for bounded convex interactions or \( N = 2 \), to provide the optimal comotion functions\cite{47-49}. On the other hand, there are cases in higher dimensions where, even for convex interactions, the optimal maps do not fit in the SGS scheme\cite{46}.

It is therefore both instructive and preparatory for the rest of this thesis to discuss the case for \( d = 1 \). Eq. (3.7) in 1D implies that

\[
\frac{d}{dx} \int_{f_i(x)}^{f_{i+1}(x)} \phi(x') dx' = 0,
\]

meaning that the chunk of density comprised between any pair of positions given by \( f_i(x) \) and \( f_{i+1}(x) \) stays constant \( \forall x \). This, together with the group properties (3.8), and to avoid any accidental clustering of the SCE state that would destroy the indistinguishability of the particles, necessarily imposes that

\[
\int_{f_i(x)}^{f_{i+1}(x)} \phi(x') dx' = 1.
\]

We illustrate this concept in fig. 3.2.

The Seidl ansatz can be built starting from the cumulant function

\[
N_e(x) := \int_{-\infty}^x \phi(x') dx',
\]

we can combine eqs. (3.14), (3.15), get an explicit form for the comotion functions\cite{16}:

\[
f_i(x) = \begin{cases} 
N_e^{-1} (N_e(x) + i - 1) & \text{if } x \leq a_i, \\
N_e^{-1} (N_e(x) + i - 1 - N) & \text{if } x > a_i.
\end{cases}
\]
with $a_i = N e^{-1}(N + 1 - i)$. From now on, $f_i$ will always represent a comotion function of the Seidl form.

In figure 3.3 we report the comotion functions for a density

$$\varrho_S(x) \approx N \sum_{i=1}^{3} g_i e^{-\frac{(x-x_0)^2}{2}}$$

(3.18)

normalized to $N = 3$ in the interval $x \in [-8, 8]$, with $g_1 = 0.5$, $g_2 = 0.7$, $g_3 = 0.3$ and $x_{0,1} = -1.5$, $x_{0,2} = 0.5$, $x_{0,3} = 3$. For each fixed $x$, one can read the position of the three particles from the plot on the right. When one electron reaches $+\infty$, it "reappears" at $-\infty$. This is represented by the two vertical asymptotes.
3.2 STRONGLY INTERACTING LIMIT AS AN OPTIMAL TRANSPORT PROBLEM

Optimal Transport is a field in Mathematics which studies the problem of transferring a mass \( \mu \) into a mass \( \nu \), while minimizing a cost function.

Despite being posed more than 250 years ago by Monge\[51\], it was not after 1942 when Kantorovich introduced a generalization to Monge’s problem, now known as Monge-Kantorovich formulation\[52\], that the field underwent a gargantuan development: in the past twenty years, interest in Optimal Transport has spawned new lines of research not only in Mathematics but also in Chemistry, Economics and Physics.

In the original formulation, assume that we are given two mass distributions, \( \mu(x) \) and \( \nu(y) \), both normalised to one in a volume \( V \). Furthermore, assume that a function \( c(x, y) \) describes the cost to be paid in order to transfer a mass element from point \( x \) to point \( y \) (e.g., in its original form the cost function would read \(|x - y|\), accounting for the fact that the further the destination, the higher the cost to pay to transfer a mass element, e.g. of soil). We aim at devising a strategy, or optimal map \( \tilde{f} \), to transport the mass \( \mu(x) \) into \( \nu(y) \), while minimising the cost:

\[
\inf_{\tilde{f}} \left\{ \int_V c(x, \tilde{f}(x)) \, d\mu \bigg| \nu(\tilde{f}(x)) = \mu(x) \quad \forall x \in V \right\},
\]

where \( d\mu = \mu(x) \, dx \) for all our purposes. Proving the existence of such maps can be a daunting task, even for the simplest cost functions (e.g., \( c(x, y) = |x - y|^p, \quad p > 0 \)).

Kantorovich therefore relaxed the problem in terms of probabilities \( \gamma(x, y) \), by computing

\[
\min_{\gamma} \left\{ \int c(x, y) \, d\gamma \bigg| \int \gamma(x, y) \, dx = \nu(y), \quad \int \gamma(x, y) \, dy = \mu(x) \right\},
\]

where again in most cases of (our) interest \( d\gamma = \gamma(x, y) \, dx \, dy \) (as we will outline in a few lines, it is often the case that we can identify \( \gamma = |\Psi|^2 \)). The minimizer of eq. (3.20) is called optimal plan, and reduces to Monge’s problem if the support of \( \gamma \) is a graph \( (x, \tilde{f}(x)) \).

Eq. (3.20) can be generalized to \( N \) mass distributions \( \mu_i \), in which case it is called multimarginal optimal transport problem

\[
\min_{\gamma} \left\{ \int c(x_1, \ldots, x_N) \, d\gamma \bigg| \pi^\#_j \gamma = \mu_j \right\}, \quad (3.21)
\]

---

\( \text{3 We use the customary shorthand notation } \pi^\#_j \gamma = \int \gamma(x_1, \ldots, x_N) \, dx_1 \ldots dx_{j-1} dx_{j+1} \ldots dx_N. \)
The strength of Kantorovich’s relaxation method lies in the fact that it admits a dual formulation, namely:

\[
\min_{\gamma} \left\{ \int c(x_1, \ldots, x_N) d\gamma \mid \pi_{j}^\# \gamma = \mu_j \right\} = \max_{u_j} \left\{ \sum_j \int u_j d\mu_j \mid \sum_j u_j(x_j) \leq c(x_1, \ldots, x_N) \right\}.
\]  

(3.22)

Being the constraint on the left hand side linear, also the dual formulation allows the problem to be solved by linear programming techniques.

The first connection between Optimal Transport and Density Functional Theory was established independently in 2012[49] and 2013[48], by recognizing that the computation of \(V_{\text{SIL}}[\rho]\) is exactly a problem of the form (3.22). Just set:

- \(c(x_1, \ldots, x_N) \equiv \frac{1}{2} \sum_{i \neq j} v_{\text{ee}}(|x_i - x_j|)\)
- \(d\gamma(x_1, \ldots, x_N) \equiv |\Psi(x_1, \ldots, x_N)|^2 dx_1 \ldots dx_N\)
- \(\mu_j(x) \equiv \frac{\rho(x)}{N} dx \quad \forall j\)

This implies that \(V_{\text{SIL}}[\rho]\) can be obtained by the maximum of the Kantorovich dual problem with \(N\) equal marginals:

\[
V_{\text{SIL}}[\rho] = \max_{u} \left\{ \int u(x) \rho(x) dx \mid \sum_{i=1}^{N} u(x_i) \leq \frac{1}{2} \sum_{i \neq j} v_{\text{ee}}(|x_i - x_j|) \right\},
\]  

(3.23)

a formulation equivalent to the Legendre transform (2.14) which, in the SIL limit, has the form

\[
V_{\text{SIL}}[\rho] = \max_{v} \left\{ \inf_{q} (\Psi | \dot{\Psi} + \sum_{i=1}^{N} v(x_i) | \Psi \rangle - \int \rho(x) v(x) dx \right\}.
\]  

(3.24)

The minimizers of eqns. (3.23) and (3.24) are connected by a simple shift according to \(u[\rho](x) = -v[\rho](x) + C[\rho]\), since the minimizer in the dual formulation is required to yield the minimum in 0, whereas the Lagrangian formulation sets the potential \(v(x)\) to 0 at infinity. When the support of \(\gamma\) is a graph, the minimizer of \(V_{\text{SIL}}[\rho]\) is Monge-type, or SCE. In the rest of this chapter, we shall always assume that the minimizers of the SIL functional are of SCE type.

### 3.3 Zero Point Oscillations

We now shift our attention to the second leading term of the expansion of \(F_\rho[\rho]\) at high couplings. Before entering the mathematical details of the computation, it is instructive to depict the physics that we are going to try to describe.
The physical assumptions behind the SCE formalism is that electrons form a system in which the kinetic energy is suppressed by an infinite interaction $O(\lambda)$. As explained in the previous sections, this lead the electrons to have deterministic positions provided by a set of $N$ comotion functions, $f_i$.

At finite couplings, Heisenberg’s principle suggests us that the electrons, being forced no more into fixed position by an infinite repulsive force, must perform zero point oscillations around the equilibrium positions provided by the comotion functions.

As argued in ref. [7], being the restoring force $O(l)$ we predict the energy associated with the oscillations to be $O(p_l)$. Therefore, we expect:

$$E_0[\varrho]\approx \lambda \min_{{E^{SCE}_{pot}[\varrho](r_1, \ldots, r_N)} + \sqrt{\lambda}E^{ZPE}[\varrho] + o(\sqrt{\lambda}), \quad \lambda \gg 1.}$$

(3.25)

The rest of this section will be devoted carry out this semi-classical analysis, following ref. [14].

To start with, rewrite $\hat{H}^\lambda[\varrho]$ as

$$\hat{H}^\lambda[\varrho] = \hat{\mathcal{T}} + \lambda E^{SCE}_{pot}[\varrho](r_1, \ldots, r_N) + \hat{\mathcal{V}}^\lambda[\varrho] - \lambda \varrho^{SCE}[\varrho].$$

(3.26)

Given that we expect small oscillations around the equilibrium position provided by $\Omega_0$, eq. (3.6), the electrons will explore a small subset of the configurations space close to $\Omega_0$, which we denote $\Omega_e$:

$$\Omega_e = \{r \in \Omega | \min_{s \in \mathbb{R}^d} |r - f(s)| < \epsilon\},$$

(3.27)

where we introduced the notation $r := \{r_1, \ldots, r_N\}$ (see fig. 3.4 for an illustration of $\Omega_e$ for the simplest case of 2 electrons in $d = 1$ for a symmetric density). Notice also that with the new notation we can write $\Omega_0(s) = \frac{1}{f(s)}$.

### 3.3.0.1 The curvilinear coordinate system

It seems natural to consider only the region $\Omega_e$ for our computation, for which we define the Hessian of $E^{SCE}_{pot}$, $H(r)$, and carry on the expansion:

$$E^{SCE}_{pot}[\varrho](r) \approx \lambda \left( E^{SCE} + \frac{1}{2}(r - f(s))^T \underbrace{H(r)}_{r=f(s)} (r - f(s)) \right)$$

$$= \lambda \left( E^{SCE} + \frac{1}{2} \sum_{i,j=1}^{dN}(r_i - f_i(s))(r_j - f_j(s)) \right).$$

(3.28)

The matrix $H(s)$ retains the information about the curvature of $E^{SCE}_{pot}(r)$ around the minimum. Its eigenvectors form the principal axes of the
paraboloid which locally approximates the behavior of $E^{\text{SCE pot}}(r)$, and suggest a natural system of coordinates.

The directions along the manifold $\Omega_0$ will exhibit $d$ null eigenvalues, as the minimum is degenerate – hence flat – along the graph $(s, f(s))$.

The directions orthogonal to $\Omega_0$ will have a total of $d(N-1)$ positive eigenvalues (since we are considering the minimum of $E^{\text{SCE pot}}(s)$ must be semi-positive definite). Therefore we collect the eigenvalues according to

$$\omega^2(s) \equiv \{0, \ldots, 0, \omega^2_{d+1}(s), \ldots, \omega^2_{dN}(s)\},$$

and the corresponding eigenvectors can be organized accordingly:

$$g(s) \equiv \{e(s), \ldots, e_d(s), e_{d+1}(s), \ldots, e_{dN}(s)\}.$$  \hspace{1cm} (3.29)

The eigenvectors are orthogonal to each other $\forall s$ since $H(s)$ is symmetric. The first $d$ eigenvectors can be identified with the basis needed to write the minimizing $s$ in eq. (3.27). The corresponding coefficients will be our first $d$ coordinates in the new framework. The remaining $d(N-1)$ coordinates can be obtained by imposing the orthogonality to the manifold $\Omega_0(s)$:

$$e_\mu(s) \cdot \frac{\partial f(s)}{\partial s_\alpha} = 0, \quad \mu \in [d+1, \ldots, dN] \subset \mathbb{N}, \quad \alpha \in [1, \ldots, d] \subset \mathbb{N}. \hspace{1cm} (3.30)$$
The first \( d \) eigenvectors and the remaining \( d(N-1) \) decompose the space \( \Omega_e \) into two orthogonal subspaces which define the new set of coordinates:

\[
\mathbf{r} = \{ r_1, \ldots, r_d, r_2, \ldots, r_d, r'_{1}, \ldots, r'_N \} \Rightarrow \{ s_1, \ldots, s_d, q_{d+1}, \ldots, q_{dN} \}
\]

The curvilinear coordinates satisfy (see also fig. 3.5)

\[
\begin{align*}
\left( \mathbf{r} - f(\mathbf{s}) \right) \cdot \frac{\partial f(\mathbf{s})}{\partial s_v} &= 0, \quad v \in [1, \ldots, d] \\
q_{\mu} &= \mathbf{e}_\mu(\mathbf{s}) \cdot (\mathbf{r} - f(\mathbf{s})), \quad \mu \in [d+1, \ldots, dN]
\end{align*}
\]

from which an explicit relation between Cartesian and curvilinear coordinate can be written as

\[
\mathbf{r} = f(\mathbf{s}) + \sum_{\mu=d+1}^{dN} q_{\mu} \mathbf{e}_\mu(\mathbf{s}).
\]

The hessian is diagonal in the coordinates \((\mathbf{s}, \mathbf{q})\) and reads \( \mathbf{H}(\mathbf{s}) = \text{diag}[\omega^2(\mathbf{s})] \). The function \( E_{\text{pot}}^{\text{SCE}} \) is then readily written as a sum of normal modes:

\[
E_{\text{pot}}^{\text{SCE}}(\mathbf{r}) \Rightarrow E_{\text{pot}}^{\text{SCE}}(\mathbf{s}, \mathbf{q}) \approx E^{\text{SCE}} + \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega^2(\mathbf{s}) q_{\mu}^2.
\]

The main advantage accomplished by this coordinate transformation lies in the fact that we have been able to switch to a coordinate system in which particles move under the effect of uncoupled harmonic interactions, with a frequency dependent on their position \( \mathbf{s} \).
Notice that in eq. (3.26) the term (3.35) is multiplied by \( \lambda \). It follows from the basic properties of quantum harmonic oscillators that the effective scale of the fluctuations around the equilibrium position (or, equivalently, the width of the envelope \( \Omega_e \)) must be \( \mathcal{O}(\lambda^{-1/4}) \). Therefore, we adjust the coordinates to take into account this scaling with \( \lambda \):

\[
(s, q) \Rightarrow (s, u) := (s, \lambda^{1/4} q),
\]

which implies

\[
l = \frac{f(s)}{\lambda^{-1/4}} + \sum_{\mu=d+1}^{dN} u\mu e\mu(s).
\]

### 3.3.0.2 The Hamiltonian in the curvilinear coordinates

The kinetic energy and the external potential in eq. (3.26) still need to be expressed in the new coordinates. To start with, we rewrite the Laplacian operator in its most general form, the Laplace-Beltrami operator\[53\]. Throughout this section, we will address the curvilinear coordinate set \((s, q)\) with the letter \(x\) and the scaled coordinates \((s, u)\) with the letter \(\tilde{x}\), unless needed otherwise:

\[
(s, q) \Rightarrow x, \quad (s, u) \Rightarrow \tilde{x}.
\]

We first define the metric tensor

\[
G_{\mu\nu}(x) := \frac{\partial r}{\partial x_\mu} \cdot \frac{\partial r}{\partial x_\nu}, \quad \mu, \nu \in [1, \ldots, dN].
\]

The Laplace-Beltrami operator reads

\[
\sum_{i=1}^{dN} \frac{\partial^2}{\partial r_i^2} = \sum_{\mu, \nu=1}^{dN} \frac{1}{\sqrt{\det G(x)}} \frac{\partial}{\partial x_\mu} \left( \sqrt{\det G(x)} \left( G^{-1}(x) \right)_{\mu\nu} \frac{\partial}{\partial x_\nu} \right).
\]

The operator (3.39) has a quite intimidating form. It is helpful in order to fix the ideas and get a feeling of how the general computation runs to consider the case of two electrons in \(d = 1\). The general case follows straightforward. In fact, we can write eq. (3.34) as

\[
l = \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} s \\ f(s) \end{pmatrix} + \frac{q}{\sqrt{1 + f'(s)^2}} \begin{pmatrix} -f'(s) \\ 1 \end{pmatrix}.
\]

The metric tensor (3.38) is therefore a 2 \(\times\) 2 matrix whose components read

\[
\begin{align*}
g_{11}(x) &= \frac{\partial r}{\partial s} \cdot \frac{\partial r}{\partial s} \\
g_{12}(x) &= \frac{\partial r}{\partial s} \cdot \frac{\partial r}{\partial q} \\
g_{21}(x) &= \frac{\partial r}{\partial q} \cdot \frac{\partial r}{\partial s} \\
g_{22}(x) &= \frac{\partial r}{\partial q} \cdot \frac{\partial r}{\partial q}
\end{align*}
\]
density functional theory for strongly correlated systems

or

\[ g_{11}(x) = 1 + f''^2 - 2q f'' \frac{f''}{\sqrt{1 + f'^2}} + q^2 \left( \frac{f'^2}{(1 + f'^2)^2} \right) \]
\[ g_{12}(x) = g_{21}(x) = 0 \]
\[ g_{22}(x) = 1 \]

In terms of the scaled coordinates \((s, u)\) the metric tensor \( \tilde{G} \) is obtained through the matrix

\[
S = \begin{pmatrix} 1 & 0 \\ 0 & \lambda^{-1/4} \end{pmatrix},
\]

from which \( \tilde{G}(\tilde{x}) = S \cdot G(s, \lambda^{-1/4}u) \cdot S \). The scaled metric tensor can be split now into contributions proportional to different orders in \( u \):

\[
\tilde{G}(\tilde{x}) = \begin{pmatrix} 1 + f'^2 / \sqrt{1 + f'^2} & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} \end{pmatrix} + \frac{u}{\lambda^{1/4}} \begin{pmatrix} -\frac{2f'^2}{\sqrt{1 + f'^2}} & 0 \\ 0 & 0 \end{pmatrix} + \frac{u^2}{\lambda} \begin{pmatrix} \frac{f'^2}{(1 + f'^2)^2} & 0 \\ 0 & 0 \end{pmatrix}.
\]

Use the fact that \( \det(\tilde{G} + A) = \det(\tilde{G}^0) \det(1 + A\tilde{G}_0^{-1}) \) to write

\[
\sqrt{\det \tilde{G}} \approx \frac{\sqrt{g_{11}(s, 0)}}{\lambda^{1/4}}
\]

\[
\frac{1}{\sqrt{\det \tilde{G}}} \approx \frac{\lambda^{1/4}}{\sqrt{g_{11}(s, 0)}}
\]

\[
\tilde{G}^{-1} \approx \begin{pmatrix} \frac{1}{g_{11}(s, 0)} & 0 \\ 0 & \sqrt{\lambda} \end{pmatrix}.
\]

Using these results in eq. (3.39) (properly modified for the coordinates \( \tilde{x} \)) provides

\[
\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} = \sqrt{\lambda} \frac{\partial^2}{\partial u^2} + o(\sqrt{\lambda}).
\]

This result can be generalized (see Appendix A), allowing us to write

\[
\tilde{T} \sim -\frac{\sqrt{\lambda}}{2} \sum_{\mu=d+1}^{dN} \frac{\partial^2}{\partial u_\mu^2} + o(\sqrt{\lambda}).
\]

Thus both the second leading term of \( E_{\text{SCE}}^{\text{pot}} \) and the kinetic energy operator \( \tilde{T} \) can be showed to be \( O(\sqrt{\lambda}) \) in the curvilinear coordinates \( \tilde{x} \). The third term, namely the difference \( \tilde{V}^\lambda - \tilde{V}^{\text{SCE}} \) cannot be showed to be \( O(\sqrt{\lambda}) \). We are therefore compelled to make such an assumption, for which we write

\[
\tilde{V}^\lambda(r) - \lambda \tilde{V}^{\text{SCE}}(r) \approx \sqrt{\lambda} \tilde{V}^{\text{ZPE}}(r) + \sum_{i=1}^{\infty} \tilde{V}_i(r).
\]
This, using eq. (3.37), implies that to leading order we should have on $\Omega_c$

$$\hat{\mathcal{V}}(r) - \lambda \hat{\mathcal{V}}^{\text{SCE}}(r) \sim \sqrt{\lambda} \hat{\mathcal{V}}^{\text{ZPE}}(f(s)), \quad \lambda \gg 1. \quad (3.51)$$

To conclude, for $\lambda \gg 1$ we have

$$\hat{\mathcal{H}}^{\text{SCE}} + \sqrt{\lambda} \left( -\frac{1}{2} \sum_{\mu=d+1}^{dN} \frac{\partial^2}{\partial u_\mu^2} + \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega_\mu(s)^2 u_\mu^2 + \hat{\mathcal{V}}^{\text{ZPE}}(f(s)) \right).$$

$$\sum_{\mu=d+1}^{dN} \frac{\partial^2}{\partial u_\mu^2} + \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega_\mu(s)^2 u_\mu^2 + \hat{\mathcal{V}}^{\text{ZPE}}(f(s))$$

The Hamiltonian $\hat{\mathcal{H}}^{\text{ZPE}}[\tilde{c}]$ describes a set of $d(N-1)$ harmonic oscillators which depend on the variable $s$ whose dynamics, however, enters to a smaller order in $\lambda$, as showed in eq. (3.49).

3.3.0.3 **Ground state of the ZPE Hamiltonian**

The ground state of $\hat{\mathcal{H}}^{\text{ZPE}}[\tilde{c}]$ will read formally as the product of ground states of single particle harmonic oscillator with frequencies $\omega_\mu(s)$

$$\Psi^{\text{ZPE}}(\tilde{x}) = \mathcal{N}(s) \prod_{\mu=d+1}^{dN} \left( \frac{\omega_\mu(s)}{\pi} \right)^{1/4} e^{-\frac{\omega_\mu(s) a_\mu^2}{2}} \quad (3.53)$$

with ground state

$$E^{\text{ZPE}}(s) = \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega_\mu(s) + \hat{\mathcal{V}}^{\text{ZPE}}(f(s)). \quad (3.54)$$

The normalization can be obtained by imposing that

$$\int ds \int du \lambda^{d-1} J(s, \lambda^{-1/4} u) \lvert \Psi^{\text{ZPE}}(\tilde{x}) \rvert^2 = 1, \quad (3.55)$$

$J$ being the Jacobian for the change of coordinates $r \mapsto x$. The fact that

$$\lim_{\lambda \to \infty} \frac{\mathcal{Q}(s)}{N}, \quad \mathcal{Q}(s) = \int du \lambda^{d-1} J(s, \lambda^{-1/4} u) \lvert \Psi^{\text{ZPE}}(\tilde{x}) \rvert^2 \quad (3.56)$$

implies that, to leading order,

$$\mathcal{N}(s) = \sqrt{\frac{\mathcal{Q}(s)}{NJ(s,0)}}. \quad (3.57)$$

At first, it might seem that something is wrong with eq. (3.54). In fact, on the right hand side we have a function of $s$ which in general will admit a non-degenerate minimum, implying that at the order $\sqrt{\lambda}$ the representability condition $\Psi \mapsto \tilde{q}$ cannot be fulfilled. Nevertheless, we still have the freedom to impose to $\hat{\mathcal{V}}^{\text{ZPE}}$ to be such that $E^{\text{ZPE}}(s) = \text{const.}, \forall s$. In other words:

$$\hat{\mathcal{V}}^{\text{ZPE}}(s, f_2(s), \ldots, f_N(s)) = \sum_{i=1}^{N} \omega^{\text{ZPE}}(f_i(s))$$

$$\sum_{\mu=d+1}^{dN} \frac{\partial^2}{\partial u_\mu^2} + \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega_\mu(s)^2 u_\mu^2 + \hat{\mathcal{V}}^{\text{ZPE}}(f(s))$$

$$= -\sum_{\mu=d+1}^{dN} \frac{\omega_\mu(s)}{2} + \text{const.} \quad (3.58)$$
This also clarifies the role of the term $\hat{V}_{ZPE}(f(s))$, namely keeping the degeneracy of $\Omega_0$ at the order $\sqrt{\lambda}$. The weight of each degenerate configuration $E_{ZPE}(s)$ will hence be proportional to the density $\rho(s)$, allowing to write

$$E_{ZPE} = \int \frac{\rho(s)}{N} \left( \frac{1}{2} \sum_{\mu=d+1}^{dN} \omega_{\mu}(s) + \hat{V}_{ZPE}(f(s)) \right) ds. \quad (3.59)$$

Finally notice that since $\hat{H}^\lambda[\rho]$ and $\hat{H}_{ZPE}[\rho]$ differ only by a constant, they have the same ground state wavefunction, allowing to write $E_0[\rho](\lambda) \sim \lambda E_{SCE}[\rho] + \sqrt{\lambda} E_{ZPE}[\rho]$. This for the generalized functional reads

$$F_\lambda[\rho] = E_0[\rho](\lambda) - \int v^\lambda(\rho)(r) \rho(r) dr \\
\sim \lambda V_{ee}^{SCE}[\rho] + \sqrt{\lambda} \int \frac{\rho(s)}{N} \sum_{\mu=d+1}^{dN} \frac{\omega_{\mu}(s)}{2} ds + o(\sqrt{\lambda}). \quad (3.60)$$

By means of the Hellman-Feynman theorem we can infer also the asymptotics for $W_\lambda[\rho]$ at high couplings. Just differentiate on both sides eq. (3.60) to obtain\(^4\)

$$V_{ee}^{\lambda}[\rho] = W_\lambda[\rho] + U_{ee}[\rho] \\
\sim V_{ee}^{SCE}[\rho] + \frac{1}{\sqrt{\lambda}} \frac{1}{2} \int \frac{\rho(s)}{N} \sum_{\mu=d+1}^{dN} \frac{\omega_{\mu}(s)}{2} ds + o(\sqrt{\lambda}). \quad (3.61)$$

3.3.0.4 On the meaning of $\Psi^{ZPE}$

In the last paragraph, we showed that the universal functional in the strongly interacting limit has an expansion in terms of powers of $\sqrt{\lambda}$:

$$\langle \Psi^\lambda[\rho] | \hat{T} + \lambda \hat{V}_{ee} | \Psi^\lambda[\rho] \rangle \sim \lambda V_{ee}^{SCE}[\rho] + \sqrt{\lambda} \left( \hat{T}^{(1/2)}[\rho] + \hat{V}_{ee}^{(1/2)}[\rho] \right).$$

$$= 2T^{(1/2)}[\rho] \quad (3.62)$$

The coefficient $2T^{(1/2)}[\rho]$ was obtained by modifying the $\lambda$-dependent Hamiltonian $\hat{H}^\lambda[\rho]$ into $\hat{H}_{ZPE}[\rho]$ and correspondingly the ground state from $\Psi^\lambda[\rho]$ to $\Psi^{ZPE}[\rho]$ to obtain the same coefficients, to leading order:

$$\langle \Psi^{ZPE}[\rho] | \hat{H}_{ZPE}[\rho] - \hat{V}_{ZPE}(f(s)) | \Psi^{ZPE}[\rho] \rangle \sim \sqrt{\lambda} \left( \hat{T}_{ZPE}[\rho] + W_{\infty}[\rho] \right), \quad (3.63)$$

\(^4\) A remark is in order. The notation $W_{\infty}[\rho]$ was originally chosen in analogy with the expansion at small couplings, eq. (2.47), for which the GL2 correction is indeed the derivative of the adiabatic connection integrand at $\lambda = 0$. The counterpart at $\lambda \to \infty$ being clearly $o$, as $W_{\lambda}$ approaches smoothly a constant, makes this an extremely misleading choice. Nevertheless, it has become customary in literature and as such will be kept throughout this thesis.
with
\[ T^{(1/2)}[\psi] = T_{ZPE}^{(1/2)}[\psi] = \mathcal{W}'[\psi] = \tilde{V}_{ee}^{(1/2)}[\psi]. \] (3.64)

It should be noted, however, that one needs to be careful when drawing conclusions while taking the expectation value of \( \hat{T} + \lambda \hat{V}_{ee} \) on the ZPE wavefunction:
\[ \langle \Psi_{ZPE}[\psi] | \hat{T} + \lambda \hat{V}_{ee} | \Psi_{ZPE}[\psi] \rangle \sim \sqrt{\lambda} \left( T_{ZPE}^{(1/2)}[\psi] + \tilde{V}_{ee,ZPE}^{(1/2)}[\psi] \right). \] (3.65)

While it is true in fact that \( \tilde{T}^{(1/2)}_{ZPE}[\psi] = \tilde{T}^{(1/2)}[\psi] \), it is not true that the same holds for the true electron-electron interaction operator. In other words, we have:
\[ \tilde{V}_{ee,ZPE}^{(1/2)}[\psi] \neq \tilde{V}_{ee}^{(1/2)}[\psi]. \] (3.67)

We believe it is better to clarify this via an example, which will be again subject of study in Chapter 6. It consists of two electrons confined in an harmonic trap with repulsive harmonic interaction. We call this system "philharmonium". The Hamiltonian reads
\[ \hat{H} = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{\omega_A^2}{2} (x_1^2 + x_2^2) - \frac{\lambda}{2} (x_1 - x_2)^2. \] (3.68)

Again, introducing a rotation of coordinates
\[ \begin{cases} R &= \frac{x_1 + x_2}{\sqrt{2}} \smallskip \cr r &= \frac{x_1 - x_2}{\sqrt{2}} \end{cases}, \] (3.69)

the Hamiltonian reads
\[ \hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial R^2} + \frac{\omega_A^2}{2} R^2 - \frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{\omega^2 - 2\lambda}{2} r^2, \] (3.70)

with a ground state given by
\[ \Psi_{\lambda}(x_1, x_2) = \left( \frac{\omega_A \sqrt{\omega^2 - 2\lambda}}{\pi} \right)^{\frac{1}{4}} e^{-\omega_A \left( x_1^2 + x_2^2 \right)} e^{-\sqrt{\frac{\omega_A^2 - 2\lambda}{4}}} (x_1 + x_2). \] (3.71)

The density coming from such a ground state is a Gaussian:
\[ \rho_{\lambda}(x) = 2 \sqrt{\frac{\omega_A}{\pi}} e^{-\bar{\omega}_A x^2}, \quad \bar{\omega}_A = \frac{2\omega_A \sqrt{\omega^2 - 2\lambda}}{\omega_A + \sqrt{\omega^2 - 2\lambda}}. \] (3.72)

It is easy now to fix the density at all \( \lambda \), since it amounts to impose that \( \bar{\omega}_A = \bar{\omega} = \text{const} \Rightarrow \omega_{\lambda} = g_{\omega}(\lambda). \) If we now expand the various
expectation values on the ground state wavefunction \((3.71)\) with \(\omega_\lambda = g_\omega(\lambda)\), we obtain

\[
\langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle \sim + \frac{\sqrt{\lambda}}{2\sqrt{2}} + \frac{\tilde{\omega}}{8} \tag{3.73}
\]

\[
\langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle \sim - \frac{\lambda}{\tilde{\omega}} + \frac{\sqrt{\lambda}}{2\sqrt{2}} \tag{3.74}
\]

\[
\langle \Psi_\lambda | \hat{V}_l | \Psi_\lambda \rangle \sim \frac{\lambda}{\tilde{\omega}} + \frac{\sqrt{\lambda}}{2\sqrt{2}} \tag{3.75}
\]

(notice the virial theorem, satisfied to all orders).

On the other hand, the function \(g\) can be expanded for large \(\lambda\) to yield

\[
g_\omega(\lambda) \sim \sqrt{2\lambda} + \frac{\tilde{\omega}^2}{8\sqrt{2\sqrt{\lambda}}} \tag{3.76}
\]

a result that can be inserted directly in \((3.71)\) to yield an approximate wavefunction, which we label \(\Psi_{ZPE}\):

\[
\Psi_{ZPE} = \left( \frac{\sqrt{\lambda} \tilde{\omega}}{\sqrt{2\pi}^2} \right)^\frac{1}{4} e^{-\frac{1}{4}\sqrt{\lambda}(x_1+x_2)^2 - \frac{1}{4}\tilde{\omega}(x_1-x_2)^2}. \tag{3.77}
\]

Using \(\Psi_{ZPE}\) to compute the expectation values, we get

\[
\langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle \sim + \frac{\sqrt{\lambda}}{2\sqrt{2}} + \frac{\tilde{\omega}}{8} \tag{3.78}
\]

\[
\langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle \sim - \frac{\lambda}{\tilde{\omega}} \tag{3.79}
\]

\[
\langle \Psi_\lambda | \hat{V}_l | \Psi_\lambda \rangle \sim \frac{\lambda}{\tilde{\omega}} + \frac{\sqrt{\lambda}}{2\sqrt{2}} \tag{3.80}
\]

So we see, comparing with eqs. \((3.73)\), that indeed the expectation values of the external potential and the interaction energy are accurate only to first order, whereas the kinetic energy is correct through order \(O(\lambda^0)\).