On the Kohn-Sham Equations with Periodic Background Potentials

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We study the question of existence and uniqueness for the finite temperature Kohn-Sham equations. For finite volumes, a unique soluion is shown to exists if the effective potential satisfies a set of general conditions and the coupling constant is smaller than a certain value. For periodic background potentials, this value is proven to be volume independent. In this case, the finite volume solutions are shown to converge as the thermodynamic limit is considered. The local density approximation is shown to satisfy the general conditions mentioned above.

1. INTRODUCTION

For a self-interacting N-body quantum system with a background potential u, the finite temperature Kohn-Sham equations consist of:

$$\begin{cases} \left(-\frac{1}{2}\Delta + u + n * v + v_{xc}[n]\right)\eta_m = \varepsilon_m \eta_m \\ n(\vec{x}) = \sum_m \left(1 + e^{\beta(\varepsilon_m - \mu)}\right)^{-1} |\eta_m(\vec{x})|^2, \end{cases} \tag{1}$$

where the value of the chemical potential is found from:

$$N = \sum_m \left(1 + e^{\beta(\varepsilon_m - \mu)}\right)^{-1}. \tag{2}$$

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The exchange-correlation potential $v_{xc}[n]$ may have a complicated functional dependence on the particle density. However, it acts on the Kohn-Sham orbitals as a regular potential, by multiplying the orbitals with a function.[1]

These equations determine the density of particles at the thermodynamic equilibrium of the system. The zero temperature formalism proposed by Hohenberg and Kohn,[2] now known as the Density Functional Theory, can be extended to finite temperatures if, instead of the ground state energy, one considers the grand canonical potential.[3] In this case, one can show that the grand canonical potential is a functional of the particle density. This functional achieves its minimum for the equilibrium particle density. Eqs. (1) and (2) represents the Euler-Lagrange equations associated with this functional.[4, 5] In contrast to the zero temperature case, the finite temperature Kohn-Sham equations involve an infinite set of orbitals. In practical applications however, one only has to consider the orbitals with energies up to $\mu + k_B T$. Above this limit, the contribution to the density of particles Eq. (2) becomes negligible. The finite temperature formalism has a major advantage over the zero temperature formalism in that it avoids the problem associated with the degeneracy of the last occupied energy level.

While most of the work on these equations has been concerned with rigorous derivations or finding better and better approximation of the exchange-correlation potential, little it is known about their solutions.[6, 7] Computational physicists often assume that the Kohn-Sham equations have a unique solution. The same assumption has been made for long time for models like Hartree or Hartree-Fock. Despite many efforts however, the uniqueness is still an open problem for these models[8] and only little advance[9–11] has been made in this direction. Moreover, the symmetry breaking within these models[12, 13] shows that the uniqueness can be a very delicate problem.

The first goal of this paper is to search for those conditions on the effective potential that guarantee the existence and uniqueness of a solution for the Kohn-Sham equations on a finite volume. The conditions will be formulated at an abstract level, without making references to any explicit expression or approximation of the exchange correlation potential. We will show in the last section that these abstract conditions are general enough to include the local density approximation.

The Kohn-Sham equations are derived from the Kohn-Hohenberg[2] functional. This functional is based on the assumption that the density of particles is v-representable. Despite many efforts, the v-representability problem has not been yet rigorously solved for infinite volume. A functional that does not require v-representability has been proposed by

Lieb.[14] Unfortunately, this new functional does not automatically lead to the Kohn-Sham equations. It was shown however that, for finite volumes, the Kohn-Hohenberg and Lieb functionals coincide.[1] The relation between the two functionals is not yet completely understood for infinite volume. The thermodynamic limit of the Kohn-Sham equations can therefore be considered as a fundamental issue in density functional theory. We believe that the unsolved part of the v-representability problem can be avoided by studying the thermodynamic limit of the finite volume Kohn-Sham equations instead of considering the infinite volume.

The second goal of this paper is to find the general conditions on the effective potential which guarantee that the finite volume solutions of the Kohn-Sham equations have a well defined thermodynamic limit. Our solution to this problem applies only for periodic background potentials.

Within the local density approximation, partial results on the Kohn-Sham equations have been reported in ref. 10. The methods developed there could not be used for realistic exchange-correlations potentials. The main obstacle was the low density behavior of realistic exchange-correlations potentials. In the last section of this paper we will show how this problem can be solved. We will show that the local density approximation of the exchange-correlation potential satisfies the abstract conditions mentioned above.

2. THE FIXED POINT APPROACH

We assume in the following that the background potential comes from the interaction of the particles with background charges of opposite sign, which are considered fixed and given. In this case, the Kohn-Sham equations take the following form:

$$
\begin{cases}
\left(-\tfrac{1}{2}\Delta + (n-n_0) * v + v_{xc}[n]\right)\eta_m = \varepsilon_m \eta_m \\
n(\vec{x}) = \sum_m \left(1 + e^{\beta(\varepsilon_m - \mu)}\right)^{-1} |\eta_m(\vec{x})|^2.
\end{cases}
\tag{3}
$$

We also consider a system which is charge neutral:

$$
\int_{\text{vol}} (n(\vec{x}) - n_0(\vec{x}))\, d\vec{x} = 0.
\tag{4}
$$

The chemical potential must be adjusted such that the above condition is satisfied. The neutrality condition will play an essential role when long range interactions are considered and it will help us to improve our previous estimates on the Hartree potential.[11] We borrowed the idea from the

homogeneous electron gas where it is known that the neutrality condition is essential when the thermodynamic limit is considered.[15] Also, the neutrality or partial neutrality condition play an essential role in the Hartree-Fock model when applied to Coulomb systems.[16, 17] The neutrality condition will be further discussed at the end of Section 3.

Let us denote the Kohn-Sham Hamiltonian and the effective potential by:

$$H_n = -\tfrac{1}{2}\Delta + \lambda V[n] \tag{5}$$
$$V[n] = (n-n_0) * v + v_{xc}[n],$$

and the Fermi-Dirac distribution by:

$$\Phi_{\mathrm{FD}}(t) = (1+e^{\beta t})^{-1}. \tag{6}$$

For finite volumes, we now formulate the Kohn-Sham equations as a fixed point problem. In this case, Δ is the Laplace operator over the volume vol constrained by various boundary conditions.

Theorem 1 (The Fixed Point Approach).   Let $S^N \subset L^1(\mathrm{vol})$ be defined as:

$$S^N = \{n \in L^1(\mathrm{vol}), \|n\|_{L^1(\mathrm{vol})} = N\}. \tag{7}$$

Suppose that for $n \in S^N$ and $a > 0$ the following condition is satisfied:

$$\|V[n](-\tfrac{1}{2}\Delta+a)^{-1}\| \leqslant \gamma_a, \tag{8}$$

where γ_a may depend on N. Then the map:

$$T: S^N \to S^N \tag{9}$$
$$S^N \ni n \to T[n](\vec{x}) = \Phi_{\mathrm{FD}}(H_n - \mu_n)(\vec{x}, \vec{x})$$

is well defined. Here, μ_n represents the unique solution of the equation:

$$N = \mathrm{Tr}\,\Phi_{\mathrm{FD}}(H_n - \mu_n). \tag{10}$$

Moreover, the fixed points of the map T generates all the solutions of the Kohn-Sham equations.

Let us prove first the following result which will be used many times in the following.

Lemma 2. Let H_0 be a self-adjoint, bounded from below Hamiltonian and suppose that $\exp(-H_0)$ is of trace class. Let V be a self-adjoint potential such that, for $a > |\inf \sigma(H_0)|$:

$$\|V(H_0 + a)^{-1}\| \leqslant \gamma_a. \tag{11}$$

Then $H = H_0 + \lambda V$ is self-adjoint and:

$$\operatorname{Tr} \phi_{j,\mu}[(1 + \lambda \gamma_a) H_0 + \lambda a \gamma_a] \leqslant \operatorname{Tr} (1 + e^{\beta(H - \mu)})^{-j}$$
$$\leqslant e^{j\beta(\mu + \lambda a \gamma_a)} \operatorname{Tr} e^{-j\beta(1 - \lambda \gamma_a) H_0}, \tag{12}$$

where $\phi_{j,\mu}$, $j = 1, 2,...$, are monotone decreasing, convex functions on $[\epsilon_0, \infty)$, $\epsilon_0 = \inf \sigma(H)$, such that:

$$\phi_{j,\mu}(t) \leqslant (1 + e^{\beta(t - \mu)})^{-j}. \tag{13}$$

All functions $\phi_{j,\mu}(t)$ can be chosen such that $\lim_{\mu \to \infty} \phi_{j,\mu}(t) = 1$ and $\phi_{j,\mu}(t) > 0$.

Proof. We will use classical techniques from ref. 18. We start with the first inequality. Let $\{\eta_m^0, \varepsilon_m^0\}_m$ be the eigenvectors and the corresponding eigenvalues of H_0. $\eta_m^0 \in \mathscr{D}(H)$ and we can write:

$$\operatorname{Tr} (1 + e^{\beta(H - \mu)})^{-j} \geqslant \operatorname{Tr} \phi_{j,\mu}(H) \geqslant \sum_m \phi_{j,\mu}(\langle \eta_m^0, H \eta_m^0 \rangle)$$

$$= \sum_m \phi_{j,\mu}((\varepsilon_m^0 + a)\langle \eta_m^0, (I + \lambda V(H_0 + a)^{-1}) \eta_m^0 \rangle - a)$$

$$\geqslant \sum_m \phi_{j,\mu}((1 + \lambda \gamma_a) \varepsilon_m^0 + \lambda a \gamma_a)$$

$$= \operatorname{Tr} \phi_{j,\mu}((1 + \lambda \gamma_a) H_0 + \lambda a \gamma_a). \tag{14}$$

For the second inequality, let $\{\eta_m, \varepsilon_m\}_m$ be the eigenvectors and the corresponding eigenvalues of H. Then:

$$e^{j\beta(a + \mu)} \operatorname{Tr} e^{-j\beta(1 - \lambda \gamma_a)(H_0 + a)} \geqslant e^{j\beta(a + \mu)} \sum_m e^{-j\beta(1 - \lambda \gamma_a)\langle \eta_m, (H_0 + a) \eta_m \rangle}$$

$$= e^{j\beta(a + \mu)} \sum_m e^{-j\beta(1 - \lambda \gamma_a)(\varepsilon_m + a)\langle \eta_m, (I + \lambda V(H_0 + a)^{-1})^{-1} \eta_m \rangle}$$

$$\geqslant e^{j\beta(a + \mu)} \sum_m e^{-j\beta(1 - \lambda \gamma_a)(\varepsilon_m + a)/(1 - \lambda \gamma_a)}$$

$$\geqslant \operatorname{Tr} (1 + e^{\beta(H - \mu)})^{-j}. \quad \blacksquare \tag{15}$$

Proof of Theorem 1. We need to show that Eq. (10) has a unique solution for all $n \in S^N$. From the previous Lemma,

$$\frac{d}{d\mu} \operatorname{Tr} \Phi_{\mathrm{FD}}(H_n - \mu) = \beta e^{-\beta\mu} \operatorname{Tr} (1 + e^{\beta(H_n - \mu)})^{-2}$$

$$\geq \beta e^{-\beta\mu} \operatorname{Tr} \phi_{2,\mu}\left(-\frac{1}{2}(1 + \lambda\gamma_a)\,\Delta + \lambda a\gamma_a\right). \quad (16)$$

The last term is strictly positive when we choose $\phi_{2,\mu} > 0$. Also, from the previous Lemma, it follows that the above derivative is finite. Then the right hand side of Eq. (10) is a strictly monotone, continuous function of μ. As we already mentioned, $\phi_{j,\mu}$ can be chosen such that $\phi_{j,\mu} \to 1$ as μ goes to $+\infty$. Then one can see from

$$\operatorname{Tr} \phi_{1,\mu}[-\frac{1}{2}(1 + \lambda\gamma_a)\,\Delta + \lambda a\gamma_a] \leq \operatorname{Tr} \Phi_{\mathrm{FD}}(H_n - \mu)$$

$$\leq e^{\beta(\mu + \lambda a\gamma_a)} \operatorname{Tr} e^{\beta/2(1 - \lambda\gamma_a)\,\Delta}, \quad (17)$$

that, as μ is varied from $-\infty$ to $+\infty$, the right hand side of Eq. (10) varies from 0 to $+\infty$. This, combined with the strict monotonicity and continuity, allows us to conclude that Eq. (10) has a unique solution. Using the eigenvectors and theeigenvalues of H_n,

$$(-\tfrac{1}{2}\Delta + (n - n_0) * v + v_{xc}[n])\,\eta_m = \varepsilon_m \eta_m, \quad (18)$$

the fixed point equation for T reduces to

$$n(\vec{x}) = \sum_m (1 + e^{\beta(\varepsilon_m - \mu_n)})^{-1} |\eta_m(\vec{x})|^2. \quad (19)$$

Equations (18) and (19) represent exactly the Kohn-Sham equations. ∎

The fixed points of the map T generates all the solutions of the Kohn-Sham equations because S^N is the largest set where these solutions can be found. Another important observation is that there exists an upper and lower limit on the chemical potential, limits which may depend in general on the number of particles. This can be seen from:

$$\operatorname{Tr} \phi_{1,\mu_n}[-\tfrac{1}{2}(1 + \lambda\gamma_a)\,\Delta + \lambda a\gamma_a] \leq N \leq e^{\beta(\mu_n + \lambda a\gamma_a)} \operatorname{Tr} e^{\beta/2(1 - \lambda\gamma_a)\,\Delta}. \quad (20)$$

For periodic background potentials however, we will show that this limits are independent of the number of particles.

3. THE KOHN-SHAM EQUATIONS WITH PERIODIC BACKGROUND POTENTIALS

In the following we consider a background charge distribution which is periodic with respect to a lattice Γ,

$$\Gamma = \left\{ \vec{x} \in R^3, \vec{x} = \sum_{i=1}^{3} n^i \vec{\delta}_i, n^i \in Z \right\}, \tag{21}$$

i.e., $n_0(\vec{x} + \vec{R}) = n_0(\vec{x})$ almost everywhere when $\vec{R} \in \Gamma$. $\vec{\delta}_i$, $i = \overline{1, 3}$, represent three linearly independent vectors in R^3. Let us also consider a finite crystal confined in the volume:

$$V = \left\{ \vec{x} \in R^3, \vec{x} = \sum_{i=1}^{3} \alpha^i \vec{\delta}_i, 0 \leqslant \alpha^i \leqslant K \right\}, \tag{22}$$

where K is a positive integer. We denote the crystal's unit cell by:

$$\text{cell} = \left\{ \vec{x} \in R^3, \vec{x} = \sum_{i=1}^{3} \alpha^i \vec{\delta}_i, 0 \leqslant \alpha^i \leqslant 1 \right\}. \tag{23}$$

Thus, the crystal is formed from K^3 unit cells. We impose periodic boundary conditions and we also allow the particles on opposite faces of the crystal to interact to each other. The resulting problem is that of particles trapped on a torus $\mathscr{T}$ obtained by connecting the opposite faces of the crystal. Any point from R^3 can be viewed as a point of the torus. The kinetic term of the Kohn-Sham Hamiltonian is given by $-\frac{1}{2}\Delta$, where Δ represents the Laplace operator over the torus $\mathscr{T}$. We will assume that the particles interact via a two-body potential which depends only on the distance between particles:

$$v(\vec{x}, \vec{y}) = v(|\vec{x}, \vec{y}|), \vec{x}, \vec{y} \in \mathscr{T}, \tag{24}$$

where $|\cdot, \cdot|$ denotes the distance on the torus. In this case, the potential generated by the background charge is Γ-periodic. Indeed, for $\vec{R} \in \Gamma$:

$$\int_{\mathscr{T}} v(|\vec{x} + \vec{R}, \vec{y}|) \, n_0(\vec{y}) \, d\vec{y} = \int_{\mathscr{T}} v(|\vec{x}, \vec{y} - \vec{R}|) \, n_0(\vec{y}) \, d\vec{y}$$

$$= \int_{\mathscr{T}} v(|\vec{x}, \vec{y}|) \, n_0(\vec{y} + \vec{R}) \, d\vec{y}$$

$$= \int_{\mathscr{T}} v(|\vec{x}, \vec{y}|) \, n_0(\vec{y}) \, d\vec{y}, \tag{25}$$

where we also used that the measure $d\vec{y}$ is invariant at translations. We will assume that the exchange-correlation potential is Γ-periodic when the density of particles is Γ-periodic. In this case, the set of Γ-periodic density of particles:

$$S_{\text{per}}^N = \{n \in S^N, n(\vec{x}+\vec{R}) = n(\vec{x}) \text{ a.e., } \vec{R} \in \Gamma\} \tag{26}$$

is invariant for the map T. In this paper, we will search for the fixed points of the map T only in this invariant set. Thus, from now on, we will restrict T to S_{per}^N. For finite volume, the above system include also the case of nonperiodic background potentials. To include such systems, the unit cell is taken equal to the entire volume. Let us denote by $N_0 = N/K^3$ the number of particles per unit cell. The thermodynamic limit is defined by fixing N_0 and letting the number of unit cells to go to infinity.

Let us consider the following unitary transformation:

$$U: L^2(\mathcal{T}) \to \bigoplus_{\mathbf{q} \in \Lambda_K} L^2[\text{cell}]$$

$$L^2(\mathcal{T}) \ni f \to \bigoplus_{\mathbf{q} \in \Lambda_K} (Uf)_{\mathbf{q}} \tag{27}$$

$$(Uf)_{\mathbf{q}}(\vec{x}) = K^{-3/2} \sum_{\mathbf{m} \in \Lambda_K} e^{-i\Sigma_{j=1}^3 m^j \theta_{\mathbf{q}}^j} f(\vec{x}+\Sigma_{j=1}^3 m^j \vec{\delta}_j),$$

where $\vec{\theta}_{\mathbf{q}} = \frac{2\pi}{K}\mathbf{q}$ and $\Lambda_K = \{0, 1, ..., K-1\}^3$. For $n \in S_{\text{per}}^N$, the Kohn-Sham Hamiltonian is Γ-periodic and consequently:[19]

$$UH_nU^{-1} = \bigoplus_{\mathbf{q} \in \Lambda_K} (-\tfrac{1}{2}\Delta_{\vec{\theta}_{\mathbf{q}}} + \lambda V[n]) \equiv \bigoplus_{\mathbf{q} \in \Lambda_K} H_n^{(\mathbf{q})}, \tag{28}$$

where $\Delta_{\vec{\theta}}$ is the Laplace operator over the unit cell with the following boundary conditions:

$$f(\vec{x}+\vec{\delta}_j) = e^{i\theta^j}f(\vec{x}) \qquad \text{and} \qquad f'(\vec{x}+\vec{\delta}_j) = e^{i\theta^j}f'(\vec{x}) \tag{29}$$

for $\vec{x}$ and $\vec{x}+\vec{\delta}_j$ on the faces of the unit cell. The symbol f' stands for the derivative of f along $\vec{\delta}_j$. $V[n]$ in Eq. (28) is just the restriction of the effective potential to the unit cell. Because the kinetic energy and the effective potential depends on the volume, we will write the Kohn-Sham Hamiltonian as:

$$H_n^{(K)} = -\tfrac{1}{2}\Delta + V^{(K)}[n]. \tag{30}$$

We will write T_K to indicate that the map defined in the previous section depends on K. Also, because $N = K^3 N_0$, it will be more convenient to use the notation S_{per}^K instead of S_{per}^N.

Let us discuss now the neutrality condition. This condition seems artificial for interactions other than the Coulomb force. However, when the volume is transformed to a torus and the particles interact via a potential which depends only on the distance between the particles, one can immediately see that adding a uniform background charge has the effect of a constant added to the Kohn-Sham Hamiltonian or to the full many-body Hamiltonian. This does not affect the solutions of the Kohn-Sham equations or the physiscs of the problem. Thus, we can allways add a uniform background charge such that the neutrality condition Eq. (4) is satisfied. The neutrality condition can be regarded as a mathematical artifact.

4. THE RESULT

Our abstract conditions for existence, uniqueness and thermodynamic limit for the Kohn-Sham equations consist of the following.

(C1)   For any $\vec{\theta} \in [0, 2\pi)^3$, $n \in S_{\mathrm{per}}^K$ and $a > 0$,

$$\|V^{(K)}[n](-\tfrac{1}{2}\Delta_{\vec{\theta}} + a)^{-1}\| \leqslant \gamma_a, \tag{31}$$

where it is assumed that γ_a depends only on a (when N_0 is kept fixed).

(C2)   There exists a closed set $B \subset L^1(\mathrm{cell})$ such that $T_K[S_{\mathrm{per}}^K] \subset B_K$, where

$$B_K = \left\{ n \in S_{\mathrm{per}}^K, \, n|_{\mathrm{cell}} \in B \right\}, \tag{32}$$

and, for $n_{1,2} \in B_K$, there exists a constant L, independent of K, such that:

$$\|V^{(K)}[n_1] - V^{(K)}[n_2]\|_{L^1(\mathrm{cell})} \leqslant L \, \|n_1 - n_2\|_{L^1(\mathrm{cell})}. \tag{33}$$

(C3)   For $n \in S_{\mathrm{per}}^K$,

$$\|V^{(K+1)}[n] - V^{(K)}[n]\|_{L^1(\mathrm{cell})} \to 0 \qquad \text{as} \quad K \to \infty, \tag{34}$$

where n in $V^{(K+1)}[n]$ represents the unique extension of n in S_{per}^{K+1}.

Our main result is given below.

Theorem 3. Suppose that (C1)–(C3) are satisfied. Then:

(i) The maps T_K are well defined.

(ii) T_K have a unique fixed point provided the coupling constant is smaller than a certain value which is independent of K.

(iii) The thermodynamic limit of the fixed points is well defined.

Because the proof of the first two points and the proof of the third point of the above Theorem are based on different techniques, we present them in two separate subsections.

4.1. Existence and Uniqueness for Finite Volume

Proof of Theorem 3. (i) Using the unitary transformation Eq. (27), for $f \in L^2(\mathcal{T})$:

$$\langle f, V^{(K)}[n](-\tfrac{1}{2}\Delta + a)^{-1} f \rangle = \sum_{\mathbf{q} \in \Lambda_K} \langle f_{\mathbf{q}}, V^{(K)}[n](-\tfrac{1}{2}\Delta_{\vec{\theta}_{\mathbf{q}}} + a)^{-1} f_{\mathbf{q}} \rangle$$

$$\leqslant \gamma_a \sum_{\mathbf{q} \in \Lambda_K} \|f_{\mathbf{q}}\|^2_{L^2(\text{cell})} = \gamma_a \|f\|^2_{L^2(\mathcal{T})}. \tag{35}$$

Thus, the conditions of Theorem 1 are uniformly satisfied and in consequence, all the maps T_K are well defined. From this uniform estimate one can easily conclude that the spectrum of $H_n^{(K, \mathbf{q})}$ is uniformly bounded from below, i.e., there exists an ϵ_0, independent of K, such that $\sigma(H_n^{(K, \mathbf{q})}) \subset [\epsilon_0, \infty)$ and, consequently, $\sigma(H_n^{(K)}) \subset [\epsilon_0, \infty)$ for all K. We can also show that the upper and lower limits of the chemical potential do not depend on the volume. Indeed, using again the unitary transformation Eq. (27), the inequalities Eq. (20) can be transformed into:

$$\inf \text{Tr} \, \phi_{1, \mu_n}(-\tfrac{1}{2}(1 + \lambda\gamma_a)\Delta_{\vec{\theta}} + \lambda a\gamma_a) \leqslant N_0 \leqslant e^{\beta(\mu_n + \lambda a\gamma_a)} \sup \text{Tr} \, e^{\beta/2(1 - \lambda\gamma_a)\Delta_{\vec{\theta}}}, \tag{36}$$

where the infimum and supremum go over all $\vec{\theta} \in [0, 2\pi)^3$. Using the explicit expressions for the eigenvalues of $\Delta_{\vec{\theta}}$ and the fact that we can chose $\phi_{1, \mu}$ such that $\lim_{\mu \to \infty} \phi_{1, \mu} = 1$, we can conclude from above that there exist μ_m and μ_M, independent of K, such that $\mu_n \in [\mu_m, \mu_M]$. For $\lambda \leqslant 1$, all these parameters, ϵ_0, μ_m and μ_M, can be considered λ independent. ∎

We prepare now for the proof of the second point of Theorem 3. Let us prove an estimate which will be used many times in the following. Along this paper, $\|\cdot\|_1$ will denote the trace norm.

Proposition 4. Let F be an analytic function in a vicinity of $[\epsilon_0, \infty)$ and V_1 and V_2 two self-adjoint potentials over the unit cell such that:

$$\|V_{1,2}\, (-\tfrac{1}{2}\Delta_{\tilde\theta} + a)^{-1}\| \leq \gamma_a. \tag{37}$$

Then,

$$\|F\,(-\tfrac{1}{2}\Delta_{\tilde\theta} + \lambda V_1) - F\,(-\tfrac{1}{2}\Delta_{\tilde\theta} + \lambda V_2)\|_1 \leq \lambda\gamma_F\, \|V_1 - V_2\|_{L^1(\text{cell})}, \tag{38}$$

where γ_F depends only on the function F.

Proof. Using the notation $\Delta V = V_1 - V_2$ and $g_{a,z}(x) = (x+a)/(x-z)$, we can write after simple manipulations:

$$
\begin{aligned}
F&\left(-\frac{1}{2}\Delta_{\tilde\theta} + \lambda V_1\right) - F\left(-\frac{1}{2}\Delta_{\tilde\theta} + \lambda V_2\right) \\
&= \frac{\lambda}{2\pi i}\int dz\, F(z)\, g_{a,z}\left(-\frac{1}{2}\Delta_{\tilde\theta} + \lambda V_1\right)\left(1 + \lambda\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1} V_1\right)^{-1} \\
&\quad\times\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1}\Delta V\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1} \\
&\quad\times\left(1 + \lambda V_2\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1}\right)^{-1} g_{a,z}\left(-\frac{1}{2}\Delta_{\tilde\theta} + \lambda V_2\right),
\end{aligned} \tag{39}
$$

where the integral is on a curve that surrounds $[\epsilon_0, \infty)$ and belongs to the analyticity domain of F. In consequence:

$$
\begin{aligned}
\left\|F\left(-\frac{1}{2}\Delta_{\tilde\theta} + V_1\right)\right.&\left. - F\left(-\frac{1}{2}\Delta_{\tilde\theta} + V_2\right)\right\|_1 \\
&\leq \frac{\lambda}{(1-\lambda\gamma_a)^2}\int |dz|\, |F(z)| \sup_{x\in[\epsilon_0,\infty)} |g_{a,z}(x)|^2 \\
&\quad\times\left\|\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1}\Delta V\left(-\frac{1}{2}\Delta_{\tilde\theta} + a\right)^{-1}\right\|_1.
\end{aligned} \tag{40}
$$

Let us consider:

$$A \equiv |\Delta V|^{1/2} \left(-\tfrac{1}{2} \Delta_{\vec{\theta}} + a\right)^{-1}, \tag{41}$$

where the square root is defined through the polar decomposition: $\Delta V = S |\Delta V|$. We can immediately see that A is a Hilbert-Schmidt operator:

$$\|AA^{\dagger}\|_1 = \int_{\text{cell}} d\vec{x} \, |\Delta V(\vec{x})(-\tfrac{1}{2} \Delta_{\vec{\theta}} + a)^{-2}(\vec{x}, \vec{x})| \leqslant k_a \, \|\Delta V\|_{L^1(\text{cell})}. \tag{42}$$

We used the fact that $(-\tfrac{1}{2} \Delta_{\vec{\theta}} + a)^{-2}(\vec{x}, \vec{x})$ can be computed explicitly and:[11]

$$\left(-\tfrac{1}{2} \Delta_{\vec{\theta}} + a\right)^{-2}(\vec{x}, \vec{x}) \leqslant k_a, \tag{43}$$

with k_a independent of $\vec{\theta} \in [0, 2\pi)^3$. Then we can continue:

$$\|(-\tfrac{1}{2} \Delta_{\vec{\theta}} + a)^{-1} \Delta V (-\tfrac{1}{2} \Delta_{\vec{\theta}} + a)^{-1}\|_1 = \|A^{\dagger}SA\|_1 \leqslant \|A^{\dagger}\|_{HS} \|SA\|_{HS}$$
$$\leqslant \|A\|_{HS}^2 = \|AA^{\dagger}\|_1, \tag{44}$$

and this, together with Eqs. (40) and (42), proves the affirmation. We can also identify γ_F:

$$\gamma_F = \frac{k_a}{(1 - \lambda\gamma_a)^2} \int |dz| \, |F(z)| \sup_{x \in [\epsilon_0, \infty)} |g_{a,z}(x)|^2. \quad \blacksquare \tag{45}$$

Proof of Theorem 3. (ii) For $n_{1,2} \in B_K$ one has:

$$\|T_K[n_1] - T_K[n_2]\|_{L^1(\mathscr{T})} \leqslant \|\Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_1}) - \Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_2})\|_1$$
$$+ \|\Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_2}) - \Phi_{\text{FD}}(H_{n_2}^{(K)} - \mu_{n_2})\|_1 \tag{46}$$

Using the monotonicity of the Fermi-Dirac statistics with respect to the chemical potential we can write:

$$\|\Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_1}) - \Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_2})\|_1$$
$$= |\text{Tr} \, \Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_1}) - \text{Tr} \, \Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_2})| \tag{47}$$

At this point we use the fact that:

$$N = \text{Tr} \, \Phi_{\text{FD}}(H_{n_1}^{(K)} - \mu_{n_1}) = \text{Tr} \, \Phi_{\text{FD}}(H_{n_2}^{(K)} - \mu_{n_2}), \tag{48}$$

so we can conclude:

$$\begin{aligned}
\|T_K[n_1] - T_K[n_2]\|_{L^1(\mathscr{T})} &\leqslant 2\,\|\Phi_{\mathrm{FD}}(H_{n_1}^{(K)} - \mu_{n_2}) - \Phi_{\mathrm{FD}}(H_{n_2}^{(K)} - \mu_{n_2})\|_1 \\
&= 2\sum_{\mathfrak{q}\,\in\,\Lambda_K} \|\Phi_{\mathrm{FD}}(H_{n_1}^{(K,\,\mathfrak{q})} - \mu_{n_2}) - \Phi_{\mathrm{FD}}(H_{n_2}^{(K,\,\mathfrak{q})} - \mu_{n_2})\|_1 \\
&\leqslant 2\lambda K^3 \gamma_\Phi\,\|V^{(K)}[n_1] - V^{(K)}[n_2]\|_{L^1(\mathrm{cell})} \\
&\leqslant 2\lambda\gamma_\Phi L\,\|n_1 - n_2\|_{L^1(\mathscr{T})}.
\end{aligned} \tag{49}$$

A simple analysis of the expression (45) shows that γ_Φ is maximum when $\mu_{n_2} = \mu_M$. γ_Φ can be also chosen λ independent for $\lambda \leqslant 1$. Thus we proved that, for λ smaller than a certain constant, independent of K, the maps T_K are contractions on the closed, invariant sets B_K. This implies that they have a unique fixed point in B_K. Because $T_K[S_{\mathrm{per}}^K] \subset B_K$, it follows that T_K have a unique fixed point over the entire S_{per}^K. ∎

We end this subsection with estimates on the chemical potential.

Proposition 5. For $\mu_{1,2} \in [\mu_m, \mu_M]$ and $n \in S_{\mathrm{per}}^K$, there exists C and C' strictly positive constants, independent of K such that:

$$C\,|\mu_1 - \mu_2| \leqslant K^{-3}\,|F_K(n, \mu_1) - F_K(n, \mu_2)| \leqslant C'\,|\mu_1 - \mu_2|, \tag{50}$$

where:

$$F_K(n, \mu) = \mathrm{Tr}\,\Phi_{\mathrm{FD}}(H_n^{(K)} - \mu). \tag{51}$$

Proof. The affirmation follows from:

$$|F_K(n, \mu_1) - F_K(n, \mu_2)| = \left|\int_{\mu_1}^{\mu_2} d\mu\,\frac{\partial F_K(n, \mu)}{\partial \mu}\right| \tag{52}$$

and from estimates on

$$\frac{\partial F_K(n, \mu)}{\partial \mu} = \beta e^{-\beta\mu}\,\mathrm{Tr}(1 + e^{\beta(H_n^{(K)} - \mu)})^{-2}. \tag{53}$$

These estimates follows from:

$$\beta e^{-\beta\mu_M}\,\mathrm{Tr}(1 + e^{\beta(H_n^{(K)} - \mu_m)})^{-2} \leqslant \frac{\partial F_K(n, \mu)}{\partial \mu} \leqslant \beta e^{-\beta\mu_m}\,\mathrm{Tr}(1 + e^{\beta(H_n^{(K)} - \mu_M)})^{-2}, \tag{54}$$

which can be reduced to:

$$\beta e^{-\beta\mu_M} \inf \mathrm{Tr}\, \phi_{2,\mu_m}\left(-\frac{1}{2}(1+\lambda\gamma_a)\,\Delta_{\vec{\theta}} + \lambda a\gamma_a\right)$$

$$\leqslant K^{-3}\frac{\partial F_K(n,\mu)}{\partial\mu} \leqslant \beta e^{-\beta\mu_m}e^{2\beta(\mu_M+\lambda a\gamma_a)} \sup \mathrm{Tr}\, e^{\beta(1-\lambda\gamma_a)\,\Delta_{\vec{\theta}}}, \qquad (55)$$

by using the unitary transformation (27) and Lemma 2. The infimum and supremum go over all $\vec{\theta} \in [0, 2\pi)^3$. We can conclude that:

$$C < K^{-3}\frac{\partial F_K(n,\mu)}{\partial\mu} < C' \qquad (56)$$

where C is strictly positive if $\phi_{2,\mu} > 0$, $C' < \infty$ and both constants do not depend on K. For $\lambda \leqslant 1$, these constants can be chosen independently of λ. ∎

Theorem 6. For any $n \in B_K$, the sequence $\{\mu_{T^{\circ m}[n]}\}_m$ converges to a unique limit.

Proof. For $n_{1,2} \in B_K$, we have successively:

$$CK^3 |\mu_{n_1} - \mu_{n_2}| \leqslant |F_K(n_1, \mu_{n_1}) - F_K(n_1, \mu_{n_2})|$$

$$= |N - F_K(n_1, \mu_{n_2})|$$

$$= |F_K(n_2, \mu_{n_2}) - F_K(n_1, \mu_{n_2})|$$

$$\leqslant \|\Phi_{\mathrm{FD}}(H_{n_2}^{(K)} - \mu_{n_2}) - \Phi_{\mathrm{FD}}(H_{n_1}^{(K)} - \mu_{n_2})\|_1$$

$$\leqslant \lambda K^3 \gamma_\Phi L \|n_1 - n_2\|_{L^1(\mathrm{cell})}. \qquad (57)$$

The affirmation follows from the fact that $\{T^{\circ m}[n]\}_m$ converges to the same limit for any $n \in S_{\mathrm{per}}^K$. ∎

4.2. The Thermodynamic Limit

For a given K, let us denote by n_K and μ_K the fixed point and the corresponding chemical potential of the map T_K. We prepare now to prove the last point of Theorem 3. We will use the following result from ref. 11.

Proposition 7. Let $\mu \in [\mu_m, \mu_M]$ and V be a self-adjoint potential such that:

$$\|V(-\tfrac{1}{2}\Delta_{\vec{\theta}} + a)^{-1}\| \leqslant \gamma_a, \qquad (58)$$

for all $\vec{\theta} \in [0, 2\pi)^3$. Then:

$$\|\Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + V - \mu) - \Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}'} + V - \mu)\|_1 \leqslant ct. \, |\vec{\theta} - \vec{\theta}'|^{\epsilon}, \qquad (59)$$

where $ct.$ and ϵ depend only on γ_a.

The thermodynamic limit of the Kohn-Sam equations will follow from the following result.

Lemma 8. With the above notations,

$$\|n_{K+1} - n_K\|_{L^1(\mathrm{cell})} \to 0 \qquad \text{as} \quad K \to \infty. \qquad (60)$$

Proof. There is a unique extension of n_K in S_{per}^{K+1} which will be denoted by the same symbol n_K. An important observation is that $n_K \in B_{K+1}$. Let us prove first that

$$\|[\Phi_{\mathrm{FD}}(H_{n_K}^{(K+1)} - \mu_K) - \Phi_{\mathrm{FD}}(H_{n_K}^{(K)} - \mu_K)](\vec{x}, \vec{x})\|_{L^1(\mathrm{cell})} \qquad (61)$$

goes to zero as K goes to infinity. Indeed, Eq. (61) can be evaluated as it follows:

$$\left\| \frac{1}{(K+1)^3} \sum_{\mathfrak{q} \in \Lambda_{K+1}} \Phi_{\mathrm{FD}}(H_{n_K}^{(K+1, \mathfrak{q})} - \mu_K)(\vec{x}, \vec{x}) \right.$$
$$\left. - \frac{1}{K^3} \sum_{\mathfrak{q} \in \Lambda_K} \Phi_{\mathrm{FD}}(H_{n_K}^{(K, \mathfrak{q})} - \mu_K)(\vec{x}, \vec{x}) \right\|_{L^1(\mathrm{cell})}$$
$$\leqslant \left[\left(\frac{K+1}{K} \right)^3 - 1 \right] N_0 + \frac{1}{(K+1)^3} \sum_{\mathfrak{q} \in \partial \Lambda_{K+1}} \|\Phi_{\mathrm{FD}}(H_{n_K}^{(K+1, \mathfrak{q})} - \mu_K)\|_1$$
$$+ \frac{1}{(K+1)^3} \sum_{\mathfrak{q} \in \Lambda_K} \|\Phi_{\mathrm{FD}}(H_{n_K}^{(K+1, \mathfrak{q})} - \mu_K) - \Phi_{\mathrm{FD}}(H_{n_K}^{(K, \mathfrak{q})} - \mu_K)\|_1, \qquad (62)$$

where $\partial \Lambda_{K+1} = \Lambda_{K+1} \setminus \Lambda_K$. The first two terms above go to zero as K goes to infinity. For the last term we use the following:

$$\|\Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + V - \mu) - \Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}'} + V' - \mu)\|_1$$
$$\leqslant \|\Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + V - \mu) - \Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + V' - \mu)\|_1$$
$$+ \|\Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + V' - \mu_K) - \Phi_{\mathrm{FD}} \, (-\tfrac{1}{2} \Delta_{\vec{\theta}'} + V' - \mu)\|_1$$
$$\leqslant \lambda \gamma_{\Phi} \, \|V - V'\|_{L^1(\mathrm{cell})} + ct. \, |\vec{\theta} - \vec{\theta}'|^{\epsilon}. \qquad (63)$$

Replacing $\vec{\theta}$ and $\vec{\theta}'$ by $2\pi\mathbf{q}/(K+1)$ and $2\pi\mathbf{q}/K$, V and V' by $V^{(K+1)}[n_K]$ and $V^{(K)}[n_K]$ and μ by μ_K, Eq. (61) follows immediately from condition (C3).

Let us denote by μ_{n_K} be the chemical potential corresponding to n_K when n_K is extended in B_{K+1}, i.e.:

$$(K+1)^3 N_0 = \text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_{n_K}). \tag{64}$$

It follows that:

$$|\mu_K - \mu_{n_K}| \to 0 \qquad \text{as} \quad K \to \infty. \tag{65}$$

Indeed, from Proposition 5,

$$C\,|\mu_K - \mu_{n_K}| \leqslant \frac{1}{(K+1)^3} |\text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K) - \text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_{n_K})|$$

$$\leqslant \left| \frac{1}{(K+1)^3} \text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K) - N_0 \right|$$

$$\leqslant \left| \frac{1}{(K+1)^3} \text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K) - \frac{1}{K^3} \text{Tr}\, \Phi_{\text{FD}}(H_{n_K}^{(K)} - \mu_K) \right|$$

$$\leqslant \|[\Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K) - \Phi_{\text{FD}}(H_{n_K}^{(K)} - \mu_K)](\vec{x}, \vec{x})\|_{L^1(\text{cell})}. \tag{66}$$

Then Eq. (65) follows from Eq. (61).

Finally,

$$\|n_{K+1} - n_K\|_{L^1(\text{cell})} = \left\| \sum_{m=1}^{\infty} (T_{K+1}^{\circ m}[n_K] - T_{K+1}^{\circ (m-1)}[n_K]) \right\|_{L^1(\text{cell})}$$

$$\leqslant (1 - 2\lambda L \gamma_\Phi)^{-1} \|T_{K+1}[n_K] - n_K\|_{L^1(\text{cell})} \tag{67}$$

and:

$$\|T_{K+1}[n_K] - n_K\|_{L^1(\text{cell})}$$

$$= \|[\Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_{n_K}) - \Phi_{\text{FD}}(H_{n_K}^{(K)} - \mu_K)](\vec{x}, \vec{x})\|_{L^1(\text{cell})}$$

$$\leqslant \|[\Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_{n_K}) - \Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K)](\vec{x}, \vec{x})\|_{L^1(\text{cell})}$$

$$+ \|[\Phi_{\text{FD}}(H_{n_K}^{(K+1)} - \mu_K) - \Phi_{\text{FD}}(H_{n_K}^{(K)} - \mu_K)](\vec{x}, \vec{x})\|_{L^1(\text{cell})}. \tag{68}$$

We already proved that the last term goes to zero as $K \to \infty$. Using the monotonicity of the Fermi-Dirac, the second last term of Eq. (68) is equal to

$$(K+1)^{-3} |F_{K+1}(n_K, \mu_{n_K}) - F_{K+1}(n_K, \mu_K)| \leqslant C' |\mu_{n_K} - \mu_K|, \qquad (69)$$

where we used the same notations as in Proposition 5. ∎

Within our conditions, we cannot prove that $\{n_K\}_K$ is a Cauchy sequence and in consequence the problem of the thermodynamic limit is not yet solved. However, using the weaker result of the above Lemma, we can prove that the density of particle converges in a distributional sense as the thermodynamic limit is considered. This will end the proof of Theorem 3.

Theorem 9. If n_K is viewed as a linear functional over $L^\infty(\text{cell})$,

$$\hat{n}_K(g) = \int_{\text{cell}} n_K(\vec{x}) \, g(\vec{x}) \, d\vec{x} \,, \qquad g \in L^\infty(\text{cell}), \qquad (70)$$

then $\{\hat{n}_K\}_K$ converges weakly in $L^\infty(\text{cell})^*$.

Proof. From Banach-Alaoglu theorem[20] one knows that the closed balls in $L^\infty(\text{cell})^*$ are compact in the weak topology. Then, because $\|\hat{n}_K\| = N_0$, it follows that the sequence $\{\hat{n}_K\}_K$ has at least one accumulation point. Due to the fact that

$$\|\hat{n}_{K+1} - \hat{n}_K\| = \|n_{K+1} - n_K\|_{L^1(\text{cell})} \xrightarrow{K \to \infty} 0, \qquad (71)$$

we can conclude that there is one and only one accumulation point. ∎

5. APPLICATION: THE LOCAL DENSITY APPROXIMATION

In the local density approximation, the effective potential becomes:

$$V[n] = (n - n_0) * v + v_{xc}(n), \qquad (72)$$

where v_{xc} is a function of n instead of a functional. The value of $v_{xc}(n)$ is equal to the exchange-correlation energy per particle of the corresponding infinite, homogeneous system. Thus, there will be no volume dependence for the exchange-correlation potential. The Hartree potential however will depend, in general, on the volume. For finite range interactions, the Hartree potential does not depend on the volume when the volume becomes larger than the range of the interaction. This case has been considered in ref. 11 when the thermodynamic limit of the Hartree model was

analyzed. We impose the following conditions on the two-body interaction and exchange-correlation potential.

(P1) The singularity of the two-body potential is at least L^2 integrable.

(P2) $v(\vec{x}) \sim |\vec{x}|^{-r}$ as $|\vec{x}| \to \infty$ with $r > 2$.

(P3) $v_{xc} : (0, \infty) \to R$ is differentiable and there exists $p \geqslant 1$ such that $t^{-1/p} v_{xc}(t)$ and $t^{1-1/p} \frac{dv_{xc}}{dt}(t)$ are uniformly bounded over $[0, \infty)$.

The conditions we imposed on the exchange-correlation include, for example, the case of an homogeneous electron gas. For this particular system, it was shown[21] that the low and high density behavior of the exchange-correlation potential is dominated by the exchange part which is proportional to $n^{1/3}$. Thus, we can choose $p = 3$ in (P3) to include this case. Let us mention that, because of this behavior, the difference $v_{xc}(n_1) - v_{xc}(n_2)$ decays much slower than $n_1 - n_2$ in the low density limit. Thus, the condition (C2) fails for this particular potential unless we can prove that the density of particles is larger than a certain strictly positive value.

5.1. Estimates on the Hartree Potential

Let us point out that it is the Hartree potential that forces on us to consider only short range interactions. If one compares the conditions (P1)–(P3) with the conditions from ref. 10, one can see an improvement because now we allow the interaction to decay as $|\vec{x}|^{-r}$ with $r > 2$ instead of 3. The neutrality condition will play an essential role here. Unfortunately, we are still unable to include the Coulomb interaction in our theory. The reason is that the Hartree potential increases too fast as the system approaches the thermodynamic limit for long range interactions.

Theorem 10. Suppose the conditions (P1) and (P2) are satisfied. Then, for $n, n' \in S_{\text{per}}^K$ and $\vec{\theta} \in [0, 2\pi)^3$ the following are true:

(i) There exists γ_a^H, independent of K or $\vec{\theta} \in [0, 2\pi)^3$, such that:

$$\|(n - n_0) * v \, (-\tfrac{1}{2} \Delta_{\vec{\theta}} + a)^{-1}\| \leqslant \gamma_a^H. \tag{73}$$

(ii) There exists L^H, independent of K or $\vec{\theta} \in [0, 2\pi)^3$, such that:

$$\|(n - n') * v\|_{L^1(\text{cell})} \leqslant L^H \|n - n'\|_{L^1(\text{cell})}. \tag{74}$$

(iii) The Hartree potential satisfies the condition (C3).

Proof. Let us divide the Hartree potential in two parts,

$$\sum_{i=1,2} \int_{\text{vol}^{(i)}} v(|\vec{x}, \vec{y}|)(n(\vec{y}) - n_0(\vec{y})) \, d\vec{y} \equiv V_H^{(1)}[n] + V_H^{(2)}[n], \tag{75}$$

where $\text{vol}^{(1)}$ contains the unit cell plus the adjacent cells and $\text{vol}^{(2)} = \mathcal{T} \setminus \text{vol}^{(1)}$. For $n, n' \in S_{\text{per}}^K$, it follows

$$\|V_H^{(1)}[n] - V_H^{(1)}[n']\|_{L^1(\text{cell})} \leqslant \mathcal{N} \sup_{\vec{y} \in \text{vol}^{(1)}} \int_{\text{cell}} d\vec{x} \, |v(|\vec{x}, \vec{y}|)| \, \|n - n'\|_{L^1(\text{cell})}. \tag{76}$$

where $\mathcal{N}$ is the number of cells in $\text{vol}^{(1)}$. The estimate makes sense because, if the singularity of the interacting potential is L^2 integrable, then it is also L^1 integrable. Moreover,

$$\|V_H^{(1)}[n]\|_{L^2(\text{cell})} \leqslant 2\mathcal{N} N_0 \sqrt{\sup \int_{\text{cell}} d\vec{x} \, |v(\vec{y}_1, \vec{x}) \, v(|\vec{x}, \vec{y}_2|)|}, \tag{77}$$

where the supremum goes over all $\vec{y}_1$ and $\vec{y}_2 \in \text{vol}^{(1)}$. Again, the estimate makes sense because the singularity of the interaction is L^2 integrable. The last inequality combined with

$$\|(-\tfrac{1}{2}\Delta_{\vec{\theta}} + a)^{-1} f\|_{L^\infty(\text{cell})} \leqslant k_a^{1/2} \, \|f\|_{L^2(\text{cell})} \tag{78}$$

from ref. 11, leads to:

$$\begin{aligned}
\|V_H^{(1)}[n] &(-\tfrac{1}{2}\Delta_{\vec{\theta}} + a)^{-1} f\|_{L^2(\text{cell})} \\
&\leqslant \|V_H^{(1)}[n]\|_{L^2(\text{cell})} \, \|(-\tfrac{1}{2}\Delta_{\vec{\theta}} + a)^{-1} f\|_{L^\infty(\text{cell})} \\
&\leqslant 2 k_a^{1/2} \mathcal{N} N_0 \sqrt{\sup_{\vec{y} \in \text{vol}^{(1)}} \int_{\text{cell}} d\vec{x} \, |v(|\vec{x}, \vec{y}|)|^2} \, \|f\|_{L^2(\text{cell})}.
\end{aligned} \tag{79}$$

For the second term we write

$$\begin{aligned}
V_H^{(2)}[n](\vec{x}) &- V_H^{(2)}[n'](\vec{x}) \\
&= \sum_{\vec{R}} \int_{\text{cell}} v(|\vec{x}, \vec{y} + \vec{R}|)(n(\vec{y}) - n'(\vec{y})) \, d\vec{y} \\
&= \sum_{\vec{R}} \int_{\text{cell}} [v(|\vec{x}, \vec{y} + \vec{R}|) - v(|\vec{x}, \vec{R}|)](n(\vec{y}) - n'(\vec{y})) \, d\vec{y}, \tag{80}
\end{aligned}$$

where the sum goes over all the sites of the crystal less the origin and its first neighbors. It is this place where we used the neutrality condition. Then:

$$|V_H^{(2)}[n](\vec{x}) - V_H^{(2)}[n'](\vec{x})|$$

$$\leqslant \sum_{\vec{R}} \sup_{\vec{x}, \vec{y} \in \text{cell}} |v(|\vec{x}, \vec{y} + \vec{R}|) - v(|\vec{x}, \vec{R}|)| \, \|n - n'\|_{L^1(\text{cell})}$$

$$\leqslant \sum_{\vec{R}} \sup_{\vec{x}, \vec{y} \in \text{cell}} |v(\vec{R} - \vec{x} + \vec{y}) - v(\vec{R} - \vec{x})| \, \|n - n'\|_{L^1(\text{cell})}, \qquad (81)$$

where the last sum goes over an infinite lattice. Denoting $\vec{\xi} = \vec{R}/R$, $R = |\vec{R}|$, it follows from condition (P2) that, for large R,

$$|v(\vec{R} - \vec{x} + \vec{y}) - v(\vec{R} - \vec{x})| = ct.R^{-r} \, ||\vec{\xi} - (\vec{x} - \vec{y})/R|^{-r} - |\vec{\xi} - \vec{x}/R|^{-r}|$$
$$\leqslant ct.R^{-r} \, ||\vec{\xi} - (\vec{x} - \vec{y})/R| - |\vec{\xi} - \vec{x}/R|| \qquad (82)$$

and using $||\vec{a} + \vec{b}| - |\vec{a} - \vec{b}|| \leqslant 2 \, |\vec{b}|$ we can conclude:

$$|v(\vec{R} - \vec{x} + \vec{y}) - v(\vec{R} - \vec{x})| \leqslant ct.R^{-r-1}. \qquad (83)$$

Thus the sum in Eq. (81) converges and we proved that there exists $L_H^{(2)}$, independent of K, such that:

$$\|V_H^{(2)}[n] - V_H^{(2)}[n']\|_{L^\infty(\text{cell})} \leqslant L_H^{(2)} \, \|n - n'\|_{L^1(\text{cell})} \qquad (84)$$

which automatically leads to:

$$\|V_H^{(2)}[n] - V_H^{(2)}[n']\|_{L^1(\text{cell})} \leqslant v_{\text{cell}} L_H^{(2)} \, \|n - n'\|_{L^1(\text{cell})}. \qquad (85)$$

At this point we use the neutrality condition. Because $n_0 \in S_{\text{per}}^K$, we can set $n' = n_0$ above and by repeating the steps of Eq. (78), we can conclude

$$\|V_H^{(2)} \, [n](-\tfrac{1}{2} \varDelta_{\vec{\theta}} + a)^{-1}\| \leqslant 2k_a^{1/2} N_0 v_{\text{cell}}^{1/2} L_H^{(2)}. \qquad (86)$$

This ends the proof of point (i) and (ii). For point (iii), we notice that the difference between $V_H^{(K)}[n]$ and $V_H^{(K+1)}[n]$ is given by:

$$\sum_{\vec{R} \in \partial \varLambda_{K+1}} \int_{\text{cell}} [v(|\vec{x}, \vec{y} + \vec{R}|) - v(|\vec{x}, \vec{R}|)](n(\vec{y}) - n_0(\vec{y})) \, d\vec{y},$$

and the sum contains a number of terms proportional to $(K+1)^2$ and R is proportional to K. Then the affirmation follows from Eq. (83). ∎

5.2. Estimates on the Exchange-Correlation Potential

Condition (P3) automatically leads to the condition (C1) for the exchange-correlation potential.

Proposition 11. For $n \in S_{per}^K$,

$$\|v_{xc}(n)(-\tfrac{1}{2}\varDelta_{\bar{\theta}}+a)^{-1}\| \leqslant \gamma_a^{xc}. \tag{87}$$

Proof.

$$\begin{aligned}
\|v_{xc}(n)\|_{L^p(\text{cell})} &= \left[\int_{\text{cell}} |n(\vec{x})^{-1/p} v_{xc}(n(\vec{x}))|^p \, n(\vec{x}) \, d\vec{x} \right]^{1/p} \\
&\leqslant \sup_{t \in R_+} t^{-1/p} v_{xc}(t) \, \|n\|_{L^1(\text{cell})}^{1/p} \\
&\leqslant N_0^{1/p} \sup_{t \in R_+} t^{-1/p} v_{xc}(t),
\end{aligned} \tag{88}$$

and using Eq. (78)

$$\begin{aligned}
&\|v_{xc}(n)(-\tfrac{1}{2}\varDelta_{\bar{\theta}}+a)^{-1} f\|_{L^2(\text{cell})} \\
&\qquad \leqslant \|v_{xc}(n)\|_{L^p(\text{cell})} \, \|(-\tfrac{1}{2}\varDelta_{\bar{\theta}}+a)^{-1} f\|_{L^q(\text{cell})} \\
&\qquad \leqslant v_{\text{cell}}^{1/2-1/p} \, \|v_{xc}(n)\|_{L^p(\text{cell})} \, \|(-\tfrac{1}{2}\varDelta_{\bar{\theta}}+a)^{-1} f\|_{L^\infty(\text{cell})} \\
&\qquad \leqslant k_a^{1/2} v_{\text{cell}}^{1/2-1/p} \, \|v_{xc}(n)\|_{L^p(\text{cell})} \, \|f\|_{L^2(\text{cell})}. \quad \blacksquare
\end{aligned} \tag{89}$$

Combining the above result with the results from the previous section, it follows that the condition (C1) is satisfied for the local density approximation of the effective potential. We can also prove directly that the map T is continuous on S_{per}^K.

Proposition 12. Let $p \geqslant 1$. Then

$$\|v_{xc}(n_1) - v_{xc}(n_2)\|_{L^p(\text{cell})} \leqslant p \sup_{t \in R_+} |t^{1-1/p} v_{xc}'(t)| \, \|n_1 - n_2\|_{L^1(\text{cell})}^{1/p}, \tag{90}$$

and consequently:

$$\begin{aligned}
\|T_K[n_1] - T_K[n_2]\|_{L^1(\mathcal{T})} \leqslant{}& 2\lambda_{\varPhi} L^H \|n_1 - n_2\|_{L^1(\mathcal{T})} \\
&+ 2\lambda_{\varPhi} p K^{3-3/p} \sup_{t \in R_+} |t^{1-1/p} v_{xc}'(t)| \, \|n_1 - n_2\|_{L^1(\mathcal{T})}^{1/p},
\end{aligned} \tag{91}$$

for $n_{1,2} \in S_{per}^K$.

Proof. For t_1, $t_2 \in R_+$

$$v_{xc}(t_1) - v_{xc}(t_2) = \int_{t_1^{1/p}}^{t_2^{1/p}} \frac{dv_{xc}}{dt^{1/p}} \, dt^{1/p}$$

$$\leqslant p \sup_{t \in R_+} |t^{1-1/p} v'_{xc}(t)| \, |t_1^{1/p} - t_2^{1/p}|$$

$$\leqslant p \sup_{t \in R_+} |t^{1-1/p} v'_{xc}(t)| \, |t_1 - t_2|^{1/p},$$

for $p \geqslant 1$. We can continue:

$$\|v_{xc}(n_1) - v_{xc}(n_2)\|_{L^p(\text{cell})}$$

$$\leqslant \left(\int_{\text{cell}} (p \sup_{t \in R_+} |t^{1-1/p} v'_{xc}(t)| \, |n_1(\vec{x}) - n_2(\vec{x})|^{1/p})^p \, d\vec{x} \right)^{1/p}$$

$$= p \sup_{t \in R_+} |t^{1-1/p} v'_{xc}(t)| \, \|n_1 - n_2\|_{L^1(\text{cell})}^{1/p}. \tag{92}$$

An important consequence of the above result is that any L^q norm with $q \leqslant p$ of $v_{xc}(n_1) - v_{xc}(n_2)$ is finite. In particular:

$$\|v_{xc}(n_1) - v_{xc}(n_2)\|_{L^1(\text{cell})} \leqslant p v_{\text{cell}}^{1-1/p} \sup_{t \in R_+} |t^{1-1/p} v'_{xc}(t)| \, \|n_1 - n_2\|_{L^1(\text{cell})}^{1/p}. \tag{93}$$

We notice that the limits on the chemical potential were based only on the condition (C1). Then, following the steps of the proof of point (ii), Theorem 3, and Proposition 4 we have successively:

$$\|T_K[n_1] - T_K[n_2]\|_{L^1(\mathcal{T})}$$

$$\leqslant 2 \sum_{\mathfrak{q} \in \Lambda_K} \|\Phi_{\text{FD}}(H_{n_1}^{(K, \mathfrak{q})} - \mu_{n_2}) - \Phi_{\text{FD}}(H_{n_2}^{(K, \mathfrak{q})} - \mu_{n_2})\|_1$$

$$\leqslant 2\lambda \gamma_\Phi (\|(n_1 - n_2) * v\|_{L^1(\mathcal{T})} + \|v_{xc}(n_1) - v_{xc}(n_2)\|_{L^1(\mathcal{T})}). \quad \blacksquare \tag{94}$$

Of course, this result is far from condition (C3) because, for realistic exchange-correlation potentials we must choose $p \geqslant 1$ above. The above result however, is the best estimate one can get on the map T if only L^1 estimates on the density of particles are used. To complete our analysis we need L^∞ estimates on the density of particles.

Lemma 13. Let A and W be two self-adjoint operators on $L^2(\text{cell})$ such that A^{-1} exists,

$$\sup_{\vec{x}, \vec{y} \in \text{cell}} |A^{-1}(\vec{x}, \vec{y})| \leqslant \chi < \infty, \tag{95}$$

and AWA is bounded. Then:

$$|W(\vec{x}, \vec{x})| \leqslant v_{\text{cell}} \chi^2 \|AWA\|. \tag{96}$$

Proof. From the above conditions it follows that

$$f(\vec{y}) = A^{-1}(\vec{y}, \vec{x}) \in L^2(\text{cell}). \tag{97}$$

Thus:

$$|W(\vec{x}, \vec{x})| = \langle f, (AWA) f \rangle \leqslant \|AWA\| \|f\|_{L^2(\text{cell})}^2 \tag{98}$$
$$\leqslant v_{\text{cell}} \chi^2 \|AWA\|. \quad \blacksquare$$

Theorem 14. For $n \in S_{\text{per}}^K$,

$$n_{\min} - ct.\lambda \leqslant \|T_K[n]\|_{L^\infty} \leqslant n_{\max} + ct.\lambda, \tag{99}$$

where:

$$n_{\min} = \frac{1}{v_{\text{cell}}} \inf_{\vec{\theta} \in [0, 2\pi)^3} \text{Tr}\, \Phi_{\text{FD}} \left(-\frac{1}{2} \Delta_{\vec{\theta}} - \mu_m \right) \tag{100}$$
$$n_{\max} = \frac{1}{v_{\text{cell}}} \sup_{\vec{\theta} \in [0, 2\pi)^3} \text{Tr}\, \Phi_{\text{FD}} \left(-\frac{1}{2} \Delta_{\vec{\theta}} - \mu_M \right).$$

and $ct.$ is K independent.

Proof. In the previous Lemma, we choose:

$$W_{\mathbf{q}} = \Phi_{\text{FD}}(H_n^{(K, \mathbf{q})} - \mu_n) - \Phi_{\text{FD}} \left(-\tfrac{1}{2} \Delta_{\vec{\theta}_{\mathbf{q}}} - \mu_n \right) \tag{101}$$

and

$$A_{\mathbf{q}} = \left(-\tfrac{1}{2} \Delta_{\vec{\theta}_{\mathbf{q}}} + a \right)^2. \tag{102}$$

In this case $A_{\mathbf{q}}^{-1}$ can be computed exactly[11] and

$$|A_{\mathbf{q}}^{-1}(\vec{x}, \vec{y})| \leqslant \frac{1}{2\pi \sqrt{2a}} \sum_{\vec{R} \in \Gamma} e^{-2a |\vec{x} - \vec{y} - \vec{R}|}. \tag{103}$$

Thus, the conditions on $A_{\mathfrak{q}}$ in the previous Lemma are satisfied. Moreover, because

$$
W_{\mathfrak{q}} = \frac{1}{2} \left(e^{-\frac{\beta}{2} H_n^{(K,\mathfrak{q})}} - e^{-\frac{\beta}{2}(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}})} \right) \cosh \left[\frac{\beta}{2} (H_n^{(K,\mathfrak{q})} - \mu_n) \right]^{-1}
$$
$$
+ \frac{1}{2} e^{\frac{\beta}{4}\Delta_{\vec{\theta}_{\mathfrak{q}}}} \left(\cosh \left[\frac{\beta}{2} (H_n^{(K,\mathfrak{q})} - \mu_n) \right]^{-1} - \cosh \left[\frac{\beta}{2} \left(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} - \mu_n \right) \right]^{-1} \right)
$$
(104)

and

$$
\cosh \left[\frac{\beta}{2} (H_n^{(K,\mathfrak{q})} - \mu_n) \right]^{-1} \left(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} + a \right)^2
$$
(105)

and

$$
\left(-\tfrac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} + a \right)^2 e^{\frac{\beta}{4}\Delta_{\vec{\theta}_{\mathfrak{q}}}}
$$
(106)

are of trace class, it follows:

$$
\|A_{\mathfrak{q}} W_{\mathfrak{q}} A_{\mathfrak{q}}\|_1 \leqslant \frac{1}{2} \left\| \cosh \left[\frac{\beta}{2} (H_n^{(K,\mathfrak{q})} - \mu_n) \right]^{-1} \left(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} + a \right)^4 \right\|
$$
$$
\times \|e^{-\frac{\beta}{2} H_n^{(K,\mathfrak{q})}} - e^{-\frac{\beta}{2}(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}})}\|_1
$$
$$
+ \frac{1}{2} \left\| \left(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} + a \right)^4 e^{\frac{\beta}{4}\Delta_{\vec{\theta}_{\mathfrak{q}}}} \right\|
$$
$$
\times \left\| \cosh \left[\frac{\beta}{2} (H_n^{(K,\mathfrak{q})} - \mu_n) \right]^{-1} - \cosh \left[\frac{\beta}{2} \left(-\frac{1}{2}\Delta_{\vec{\theta}_{\mathfrak{q}}} - \mu_n \right) \right]^{-1} \right\|_1.
$$
(107)

Using Proposition 5, we can continue:

$$
\|A_{\mathfrak{q}} W_{\mathfrak{q}} A_{\mathfrak{q}}\|_1 \leqslant \frac{\lambda}{2} \left\{ \frac{\gamma_{F_1}}{(1 - \lambda\gamma_a)^4} \sup_{x \in [\epsilon_0, \infty)} (x + a)^4 \cosh \left[\frac{\beta}{2} (x - \mu_n) \right]^{-1} \right.
$$
$$
\left. + \gamma_{F_2} \sup_{x \in [0, \infty)} (x + a)^4 e^{-\frac{\beta}{2}(x - \mu_n)} \right\} \|V^{(K)}[n]\|_{L^1(\text{cell})},
$$
(108)

where $F_1(z) = e^{-\frac{\beta}{2}z}$ and $F_2(z) = \cosh[\frac{\beta}{2}(z - \mu_n)]^{-1}$. Moreover,

$$
\|V^{(K)}[n]\|_{L^1(\text{cell})} \leqslant 2N_0 L^H + v_{\text{cell}}^{1-1/p} \|v_{xc}(n)\|_{L^p(\text{cell})}
$$
$$
\leqslant 2N_0 L^H + N_0^{1/p} v_{\text{cell}}^{1-1/p} \sup_{t \in R_+} t^{-1/p} v_{xc}(t).
$$

Because $\mu_n \in [\mu_m, \mu_M]$, we can conclude that

$$\|A_{\mathbf{q}} W_{\mathbf{q}} A_{\mathbf{q}}\| \leqslant \|A_{\mathbf{q}} W_{\mathbf{q}} A_{\mathbf{q}}\|_1 \leqslant ct.\lambda, \tag{109}$$

where $ct.$ is independent of $\mathbf{q}$ or K. Consequently, $\|W_{\mathbf{q}}\|_{L^\infty(\text{cell})} \leqslant ct.\lambda$, where $ct.$ is again independent of $\mathbf{q}$ or K. Then the affirmation follows from

$$\|T_K[n] - (1 + e^{\beta(-\frac{1}{2}\Delta - \mu_n)})^{-1}(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})}$$
$$= \left\| K^{-3} \sum_{\mathbf{q} \in \Lambda_K} W_{\mathbf{q}}(\vec{x}, \vec{x}) \right\|_{L^\infty(\text{cell})} \leqslant ct.\lambda \tag{110}$$

and

$$\|\Phi_{\text{FD}}(-\tfrac{1}{2}\Delta - \mu_n)(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})}$$
$$- \|T_K[n] - \Phi_{\text{FD}}(-\tfrac{1}{2}\Delta - \mu_n)(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})}$$
$$\leqslant \|T_K[n]\|_{L^\infty} \leqslant \|\Phi_{\text{FD}}(-\tfrac{1}{2}\Delta - \mu_n)(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})}$$
$$+ \|T_K[n] - \Phi_{\text{FD}}(-\tfrac{1}{2}\Delta - \mu_n)(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})}, \tag{111}$$

by observing that

$$n_{\min} \leqslant \|\Phi_{\text{FD}}(-\tfrac{1}{2}\Delta - \mu_n)(\vec{x}, \vec{x})\|_{L^\infty(\mathscr{T})} \leqslant n_{\max}. \quad \blacksquare \tag{112}$$

Let us now return to the last condition (C2) which remains to verified. We define the set B as a the strip in $L^\infty(\text{cell})$:

$$B = \left\{ n \in L^\infty(\text{cell}), n_{\min} - \varepsilon \leqslant n \leqslant n_{\max} + \varepsilon, \text{ a.e.} \right\}, \tag{113}$$

where ε is a positive constant such that $n_{\min} > \varepsilon$. Observing that $v_{xc}'(t)$ is bounded over $I = [n_{\min} - \varepsilon, n_{\max} + \varepsilon]$, it follows:

$$\|v_{xc}(n_1) - v_{xc}(n_2)\|_{L^1(\text{cell})} = \int_{\text{cell}} \left| \int_{n_1(\vec{x})}^{n_2(\vec{x})} \frac{dv_{xc}(t)}{dt} \right| d\vec{x}$$
$$\leqslant \int_{\text{cell}} \sup_{t \in I} |v_{xc}'(t)| \, |n_1(\vec{x}) - n_2(\vec{x})| \, d\vec{x}$$
$$\leqslant \sup_{t \in I} |v_{xc}'(t)| \, \|n_1 - n_2\|_{L^1(\text{cell})}. \tag{114}$$

where we omitted a set of zero measure where $n(\vec{x})$ can have values which are not in the interval I. For λ smaller than a certain value, independent of K, it follows from Theorem 14 that $T_K[S_{\text{per}}^K] \subset B_K$ which completes our analysis of the local density approximation.

ACKNOWLEDGMENTS

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