# Periodicity of the infinite-volume ground state of a one-dimensional quantum model

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March 27, 2000

**Abstract**

We study a one-dimensional molecular system consisting of $N$ nuclei and $N$ electrons, modeled by a quantum mechanical model, namely the Thomas-Fermi-von Weizsäcker (TFW) model. For each $N$ fixed, we consider the ground state of this system. Then we investigate its behavior in the limit $N \to \infty$. We show that the system converges to a periodic system, and that its energy per atom converges to the energy of a periodic TFW model. This implies that for any periodic configuration of nuclei (with an arbitrary number $n$ of identical atoms per cell), the minimum of energy per atom is reached for the periodic configuration with *one* atom per cell.

# 1 Introduction

It is an unsolved problem in the study of matter to understand why matter is in a crystalline state at low temperature [14]. So far as we know, this "crystal problem" has been tackled by Radin [13, 8] in a classical framework and in one dimension. Our aim here is to address the same kind of problem when we take into account the quantum feature of the electrons.

We consider a set of $N$ identical pointwise nuclei, of charge $+1$ and positions $\{X_i\}_{1\leq i\leq N}$, together with $N$ electrons, defined through their density $\rho$. We assume that the system is in its ground state, which means that it is a solution of:

$$I_N = \inf\left\{E^{TFW}(\rho, \{X_i\}),\ \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}),\ |x|\rho \in L^1(\mathbf{R}),\ \int_{\mathbf{R}} \rho = N\right\}, \qquad (1.1)$$

where the energy $E^{TFW}$ is defined by:

$$\begin{aligned} E^{TFW}(\rho, \{X_i\}) &= \int_{\mathbf{R}} (\sqrt{\rho}\,')^2 + \int_{\mathbf{R}} \rho^p + \sum_{i=1}^{N} \int_{\mathbf{R}} \frac{1}{2}|x - X_i|\rho(x)dx \\ &- \frac{1}{4} \iint_{\mathbf{R}^2} \rho(x)|x-y|\rho(y)dxdy - \sum_{i<j} \frac{|X_i - X_j|}{2}. \end{aligned} \qquad (1.2)$$

The potential $-\frac{|x|}{2}$ is the Coulombic interaction potential in one dimension, and the exponent $p$ is strictly greater than one. Note that since the term $\int \rho^p$ is a homogeneous gas approximation of the kinetic energy, $p$ should be equal to $\frac{d+2}{d} = \frac{1+2}{1} = 3$ in this one-dimensional model. On the other hand, if one considers that we deal with a three-dimensional model which is invariant with respect to two variables, then $p$ should be equal to $\frac{5}{3}$. Both cases are contained in the present study. The minimization problem (1.1) with respect to $\rho$, with $\{X_i\}$ fixed, is called the electronic problem:

$$I(\{X_i\}) = \inf\left\{E^{TFW}(\rho, \{X_i\}),\ \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}),\ |x|\rho \in L^1(\mathbf{R}),\ \int_{\mathbf{R}} \rho = N\right\}, \qquad (1.3)$$

The global one, also equal to

$$I_N = \inf\left\{I(\{X_i\}), \quad X_i \in \mathbf{R}\right\}, \qquad (1.4)$$

is called the geometry optimization problem. The first point is, one can reorder the nuclei so that $X_i \leq X_{i+1}$, for all $i \in \{1, \ldots, N-1\}$. Next, a straightforward adaptation of [1] (see also [2]) shows that the electronic problem (1.3) is convex with respect to $\rho$, and has a unique solution. Also, adapting the proofs of [7] to this one-dimensional case, one easily shows that the geometry optimization problem (1.1) has a solution. Our interest lies in showing that in the limit $N \to \infty$, the system converges (in some sense to be made precise below) to a periodic system. For this purpose, we introduce the following periodic geometry optimization problem:

$$I_{per} = \inf\left\{E^{TFW}_{per,R}(\rho), \quad R > 0, \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0, R[), \quad \int_0^R \rho = 1\right\}, \qquad (1.5)$$

where $H^1_{per}(]0,R[)$ is the set of $H^1_{loc}$ functions which are periodic of period $R$, and the energy $E^{TFW}_{per,R}$ is defined by:

$$E^{TFW}_{per,R}(\rho) = \int_{-\frac{R}{2}}^{\frac{R}{2}} (\sqrt{\rho}\,')^2 + \int_{-\frac{R}{2}}^{\frac{R}{2}} \rho^p - \int_{-\frac{R}{2}}^{\frac{R}{2}} G_R(x)\rho(x)dx$$
$$+\frac{1}{2}\int_{-\frac{R}{2}}^{\frac{R}{2}}\int_{-\frac{R}{2}}^{\frac{R}{2}} \rho(x)G_R(x-y)\rho(y)dxdy, \tag{1.6}$$

where the potential $G_R$ represents the coulombic interaction between neutral $R$-periodic distribution of charges. Actually, we have:

$$G_R(x) = \sum_{k\neq 0} R\frac{e^{\frac{2i\pi kx}{R}}}{4\pi^2k^2}. \tag{1.7}$$

Here again, the minimization problem (1.5) may be splitted into electronic and geometry optimization problem, namely:

$$I_{per,R} = \inf\left\{ E^{TFW}_{per,R}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0,R[), \quad \int_0^R \rho = 1\right\}, \tag{1.8}$$

$$I_{per} = \inf\left\{ I_{per,R}\,, \quad R > 0\right\}. \tag{1.9}$$

As shown in [2], problem (1.8) is convex with respect to $\rho$ and has a unique solution $\rho_R$. Moreover, (1.9), has at least one solution $\overline{R}$, by [3].

Our first result is the convergence in energy:

**Theorem 1.1** *The sequence $\frac{I_N}{N}$ which models the energy per atom converges to the periodic energy $I_{per}$.*

Next, we show a convergence result on the electronic density and on the nuclei positions:

**Theorem 1.2** *Let $(\rho_N, \{X_i^N\})$ be any solution of problem (1.1). Then there exists a sequence $(i_N)_{N\in\mathbf{N}}$ such that:*

*(i)* $i_N \longrightarrow \infty, \quad N - i_N \longrightarrow \infty,$

*(ii) There exists a solution $(\rho_R, R)$ of (1.5) such that $\forall j \in \mathbf{Z}, \quad X^N_{i_N+j} - X^N_{i_N} \longrightarrow jR$, and $\rho_N(\cdot - X^N_{i_N}) - \rho_R(\cdot - X^N_{i_N})$ converges to 0 uniformly on any compact subset of $\mathbf{R}$.*

Note that it will become clear in the course of the proof of Theorem 1.2 (Section 4) that condition (i) is in fact a necessary condition, implied by (ii).

Before entering the details of the proofs, let us point out that similar results were obtained by Gardner and Radin [8, 12] in a classical framework, where the atoms are supposed to interact with each other through a Lennard-Jones type two-body potential. In the same spirit, Nijboer and Ventevogel [16, 10, 11] obtained an analogous result to that of Corollary 5.1 (see below) in this case. In [12], Radin also proves that a ground state configuration of $N$ particles, in the limit $N \to \infty$, is indeed a ground state in a local sense: assuming that the energy of the system $\mathcal{S}$ is defined by a density of energy $e(\mathcal{S})$, an infinite system $\mathcal{S}$ is a local ground state if for any interval $I$ and any system $\mathcal{T}$ equal to $\mathcal{S}$ on $\mathbf{R} \setminus I$, we have:

$$\int_I e(\mathcal{T}) \geq \int_I e(\mathcal{S}).$$

In the present case, the existence of $e$, i.e the local feature of the energy, is not that obvious because of the electrostatic terms, although it may be re-written in a local form (this is in fact what is done in the proof of Theorem 1.1).

# 2 A priori estimates

We first show that two nuclei can never have the same position, and study the Euler-Lagrange equations of problem (1.1).

**Proposition 2.1** *The minimization problem (1.1) has at least one solution $(\rho_N, \{X_i^N\})$. Without loss of generality, we may assume that this solution satisfies $X_i^N \leq X_{i+1}^N$, for all $1 \leq i \leq N-1$. Moreover, any such solution satisfies:*

$$X_1^N < X_2^N < \cdots < X_N^N, \quad \text{and}$$

$$\int_{X_i^N}^{X_{i+1}^N} \rho_N = 1, \quad \int_{-\infty}^{X_1^N} \rho_N = \int_{X_N^N}^{\infty} \rho_N = \frac{1}{2}. \tag{2.1}$$

**Proof:** Consider any solution of (1.1), which we denote by $(\rho_N, \{X_i^N\})$. In particular, $\rho_N$ is the solution of the minimization problem with $\{X_i^N\}$ fixed. It consequently satisfies the Euler-Lagrange equation of the corresponding problem, namely, setting $u_N = \sqrt{\rho}_N$:

$$-u_N'' + p u_N^{2p-1} + \left( \frac{1}{2} \sum_{i=1}^N |x - X_i^N| - \frac{1}{2} |x| \star u_N^2 \right) u_N + \theta u_N = 0,$$

where $\star$ denotes the convolution product over $\mathbf{R}$, and $\theta$ is the Lagrange multiplier associated to the constraint $\int_{\mathbf{R}} \rho_N = N$. Using Harnack inequality, one then easily shows that $u_N$ never cancels. Moreover, since $\sqrt{\rho}_N \in H^1(\mathbf{R})$, $\rho_N$ is a continuous and bounded function. Next, differentiating the function $E^{TFW}$ with respect to $X_i^N$ on the set $\{X_1^N < \cdots < X_N^N\}$, one finds :

$$\frac{\partial E^{TFW}}{\partial X_i^N}(\rho_N, \{X_i^N\}) = \frac{1}{2} \int_{\mathbf{R}} \operatorname{sgn}(X_i^N - x) \rho_N(x) dx - \frac{1}{2} \sum_{j=1}^N \operatorname{sgn}(X_i^N - X_j^N), \tag{2.2}$$

where sgn denotes the sign function, with the convention that $\operatorname{sgn}(0) = 0$. Since $X_i^N < X_{i+1}^N$, $\frac{1}{2} \sum_{j=1}^N \operatorname{sgn}(X_i^N - X_j^N) = i - \frac{N+1}{2}$. Hence, one easily finds that

$$\frac{\partial^2 E^{TFW}}{\partial {X_i^N}^2} = \rho_N(X_i^N), \quad \frac{\partial^2 E^{TFW}}{\partial X_i^N \partial X_j^N} = 0 \quad i \neq j.$$

This in particular shows that $E^{TFW}$ is strictly convex with respect to $\{X_i^N\}$. Next, consider the system $\{Y_i\}$ defined by (2.1): it satisfies $Y_i < Y_{i+1}$, and it is a critical point of $E^{TFW}(\rho_N, \cdot)$. Hence, it is the unique solution of the convex variational problem defining $\{X_i^N\}$. As a consequence, $X_i^N = Y_i$, hence $X_i^N < X_{i+1}^N$, for all $i$, and $(\rho_N, \{X_i^N\})$ satisfies (2.2), for all $i$. Summing these inequalities, we find (2.1). $\diamondsuit$

Studying the Euler-Lagrange equation satisfied by $\rho_N$, we define

$$\phi_N = \frac{1}{2}\rho_N \star |x| - \frac{1}{2}\sum_{i=1}^{N} |x - X_i^N| - \theta, \tag{2.3}$$

and thus have:

$$\begin{cases} -u_N'' + p u_N^{2p-1} - \phi_N u_N = 0, \\ -\phi_N'' = \sum_{i=1}^N \delta_{X_i^N} - u_N^2. \end{cases} \tag{2.4}$$

**Proposition 2.2** *For any $(\rho_N = u_N^2, \{X_i^N\})$ solution of (1.1), denoting by $\phi_N$ the function defined in (2.3), $u_N \in C^2(\mathbf{R})$, $\phi_N \in C^\infty(\mathbf{R} \setminus \{X_i^N\})$, and $\phi_N$ admits left and right derivatives at $X_i^N$, which satisfy:*

$$\forall i, \quad \phi_N'(X_i^{N^-}) = -\phi_N'(X_i^{N^+}) = \frac{1}{2}. \tag{2.5}$$

*Moreover,*

$$\frac{1}{2}{\phi_N'}^2 + \rho_N^p = \phi_N \rho_N + {u_N'}^2. \tag{2.6}$$

**Proof:** The regularity of $u_N$ and $\phi_N$ follow from standard elliptic regularity and equations (2.4). Let $x \in ]-\infty, X_1^N[$. According to (2.4), $\phi_N'(x) = \int_{-\infty}^x u_N^2(t)dt$, so that using (2.1), $\phi_N'(X_1^{N^-}) = \frac{1}{2}$. Due to the presence of a Dirac mass at $X_1^N$, one immediately deduces that $\phi_N'(X_1^{N^+}) = -\frac{1}{2}$. Next, we carry on this integration procedure until $X_2^N$, then $X_3^N$, and so on, to finally get (2.5). We then turn to the proof of (2.6): multiplying the first equation of (2.4) by $u_N'$ and the second one by $\phi_N'$, we substract the results and get, on each interval $]X_i^N, X_{i+1}^N[$:

$$-u_N'' u_N' + p u_N^{2p-1} u_N' - \phi_N u_N u_N' + \phi_N' \phi_N'' = u_N^2 \phi_N',$$

which implies:

$$\left(-\frac{1}{2}{u_N'}^2 + \frac{1}{2}u_N^{2p} + \frac{1}{4}{\phi_N'}^2 - \frac{1}{2}\phi_N u_N^2\right)' = 0.$$

Its derivative being identically 0, this function is thus a constant on each interval $]X_i^N, X_{i+1}^N[$. Moreover, since $u_N'$, $u_N$, $\phi_N$ are continuous, and since, according to (2.5), $(\phi_N')^2$ is continuous at $X_i^N$, $-{u_N'}^2 + u_N^{2p} + \frac{1}{2}{\phi_N'}^2 - \phi_N u_N^2$ is constant on $\mathbf{R}$. To show that this constant is 0, we only need to show that $\lim_{-\infty}(-{u_N'}^2 + u_N^{2p} + \frac{1}{2}{\phi_N'}^2 - \phi_N u_N^2) = 0$. In order to do so, we point out that $u_N \to 0$ at infinity since $u_N \in H^1(\mathbf{R})$. Next, writing $\phi_N'(x) = \int_{-\infty}^x u_N^2(t)dt$, one easily shows that the same property holds for $\phi_N'$. Next, we point out that, for $x \leq y < X_1^N$,

$$\phi_N(y) - \phi_N(x) = \int_x^y \int_{-\infty}^t u_N^2(s)dsdt = (y-x)\int_{-\infty}^x u_N^2 + \int_x^y (y-t)u_N^2(t)dt,$$

So that, using the fact that $|x|u_N^2 \in L^1(\mathbf{R})$,

$$|\phi_N(y) - \phi_N(x)| \leq \int_{-\infty}^{y} |t-y|u_N^2(t)dt \longrightarrow 0 \quad \text{as} \quad y \to -\infty.$$

This implies that $\phi_N$ has a limit at infinity, hence is bounded on a neighborhood of $-\infty$. Hence $\phi_N u_N$ vanishes at $-\infty$, and from the first equation of (2.4), ${u_N''}^2$ is integrable on a neighborhood of $-\infty$. Hence, $u_N'$ goes to 0 at $-\infty$. $\Diamond$

**Corollary 2.3** *Let $(\rho_N, \{X_i^N\})$ be a solution of (1.1), and $\phi_N$ be the effective potential (2.3). Then we have:*

*(i) $|\phi_N'| \leq \frac{1}{2}$, and this value is reached only at the $X_i^N$s,*

*(ii) $\rho_N \leq \left(\frac{1}{8(p-1)}\right)^{1/p}$,*

*(ii) $X_{i+1}^N - X_i^N \geq \left(8(p-1)\right)^{1/p}$, for all $i \in \{1, \ldots, N-1\}$.*

**Proof:** Since $\phi_N$ satisfies the second equation of (2.4), $\phi_N''$ is strictly positive on each $]X_i^N, X_{i+1}^N[$, which means that $\phi_N'$ is strictly increasing on these intervals, and thus ranges from $-\frac{1}{2}$ to $\frac{1}{2}$ monotonically. Next, on $]-\infty, X_1^N[$, using the fact that $\phi_N'(x) = \displaystyle\int_{-\infty}^{x} u_N^2(t)dt$, we find that $\phi_N'$ ranges monotonically from 0 to $\frac{1}{2}$ on this interval. Using the same kind of argument on $]X_N^N, \infty[$, this proves (i). We turn to the proof of (ii): $u_N$ is a $C^2$ bounded function vanishing at infinity. Hence, there exists a point $x_0 \in \mathbf{R}$ which the maximum of $u_N$. Moreover, at this point, $u_N'$ cancels and $u_N''$ is non-positive. Hence, $\phi_N(x_0)\rho_N(x_0) \geq p\rho_N^p(x_0)$, and $\frac{1}{2}{\phi_N'}^2(x_0) + \rho_N^p(x_0) = \phi_N(x_0)\rho_N(x_0)$. It follows that:

$$(p-1)\rho_N^p(x_0) \leq \frac{1}{2}{\phi_N'}^2(x_0). \tag{2.7}$$

Using (i), this implies (ii). Then, using (2.1), we have $\|\rho\|_{L^\infty}(X_{i+1} - X_i) \geq \int_{X_i}^{X_{i+1}} \rho = 1$, from which (iii) follows. $\Diamond$

**Proposition 2.4** *Let $(u_N^2, \{X_i^N\})$ be a solution of (1.1), and $\phi_N$ the corresponding effective potential (2.3). Let $(i_N)_{N\in\mathbf{N}}$ a sequence of indexes (such that $0 \leq i_N \leq N$). Then, for any $L > 0$, there exists a constant $C_L$ independent of $N$ such that*

$$\|\phi_N\|_{L^\infty(X_{i_N}^N - L, X_{i_N}^N + L)} \leq C_L \tag{2.8}$$

**Proof:** Let $J_N$ denote the interval $[X_{i_N}^N - L, X_{i_N}^N + L]$. The first step of the proof is to show that $u_N'$ is bounded. Indeed, let $x_0$ be the point where it reach its maximum (since $u_N' \longrightarrow 0$ at infinity, as the proof of Proposition 2.2 shows, such a point exists). Then $u_N''(x_0) = 0$, so that using (2.4), $\phi_N\rho_N = p\rho_N^p$. Hence, using (2.6), one finds that

$$(u_N')^2(x_0) = (1-p)\rho_N^p(x_0) + \frac{1}{2}(\phi_N')^2(x_0) \leq \frac{1}{8},$$

which proves our claim. We next show (2.8). Such a bound clearly holds for a general $C_L$ depending on $N$, since $\phi_N$ has a limit at infinity and satisfies the second equation of (2.4). We now assume that it does not hold uniformly with respect to $N$. We then have an interval $[a,b] \subset J_N$ on which $|\phi_N| \longrightarrow \infty$ as $N \to \infty$. Since $\phi_N'$ is bounded independently of $N$, either $\phi_N \longrightarrow +\infty$ on $J_N$, or $\phi_N \longrightarrow -\infty$ on the whole interval $J_N$. We now set $\overline{\phi}_N = \frac{1}{2L}\int_{J_N} \phi_N$. We then have

$$\|\phi_N - \overline{\phi}_N\|_{L^\infty(J_N)} \leq \|\phi_N'\|_{L^\infty(J_N)} \leq \frac{1}{2}.$$

Hence, $\overline{\phi}_N \rho_N = \frac{1}{2}{\phi_N'}^2 + \rho_N^p - {u_N'}^2 - (\phi_N - \overline{\phi}_N)\rho_N$ is bounded on $J_N$. As a consequence,

$$\rho_N \longrightarrow 0 \quad \text{in} \quad L^\infty(J_N).$$

This also implies that $u_N'$ and $u_N''$ converge to 0 in $\mathcal{D}'(J_N)$. Using (2.4), this implies that $\phi_N u_N \longrightarrow 0$ in $\mathcal{D}'(J_N)$. A similar result then holds for $\phi_N \rho_N$. Using (2.6), we then have

$$\frac{1}{2}{\phi_N'}^2 - {u_N'}^2 \longrightarrow 0 \quad \text{in} \quad \mathcal{D}'(J_N).$$

On the other hand, $2(u_N u_N'' + {u_N'}^2) = \rho_N'' \longrightarrow 0$ in $\mathcal{D}'(J_N)$. Since we already know that $u_N u_N'' = p u_N^{2p} - \phi_N \rho_N$ satisfies this property, we deduce that

$${\phi_N'}^2 \longrightarrow 0 \quad \text{in} \quad \mathcal{D}'(J_N).$$

This contradicts the fact that $\phi_N'' + \delta_{X_i^N} = \rho_N \longrightarrow 0$ in $L^\infty([X_{i_N}^N - \varepsilon, X_{i_N}^N + \varepsilon])$ for any $0 < \varepsilon < (8(p-1))^{1/p}$. $\diamondsuit$

**Remark 2.5** *Note that in the case where $1 < p \leq 2$, it is possible to adapt the technics used in [15] to show that there exists a constant $C$ independent of $N$ such that $|\phi_N| \leq C$ on the whole real line.*

# 3 Convergence of the energy

We start by showing that the energy per atom does converge to some real number:

**Proposition 3.1** *Let $I_N$ be defined by (1.1). Then the sequence $\frac{I_N}{N}$ converges.*

**Proof:** The point is that the sequence $I_N$ satisfies:

$$I_{N+P} < I_N + I_P, \quad \forall N, P \in \mathbf{N}. \tag{3.1}$$

This follows from an easy adaptation of the proofs of [7] or [3], and consists roughly in pointing out that if a system of $N+P$ atoms divides into two parts of respectively $N$ and $P$ atoms, its energies converges to the sum of the energy of the subsystems. Then, fixing a $P \in \mathbf{N}$, we have, for all $N \in \mathbf{N}$, $N = PQ + R$, with $R < P$. Using (3.1), we infer:

$$I_N < Q I_P + I_R.$$

Hence, $\frac{I_N}{N} < \frac{Q I_P}{PQ+R} + \frac{I_R}{N}$. Letting $N$ go to infinity, we get: $\limsup \frac{I_N}{N} \leq \frac{I_P}{P}$. We deduce from this that $\limsup \frac{I_N}{N} \leq \liminf \frac{I_N}{N}$. $\diamondsuit$

We are now in position to prove Theorem 1.1:

**Proof of Theorem 1.1:**We first show that:

$$\lim_{N\to\infty} \frac{I_N}{N} \leq I_{per}, \tag{3.2}$$

where $I_{per}$ is defined in (1.5). Consider $\overline{R} \in \mathbf{R}$ a solution of $I_{per}$, and define $Y_i^N = (i-N)\overline{R}, \quad i = 1, \ldots, 2N$. Consider the density $\rho_N = \eta_N$ solution of the electronic problem with nuclei $Y_i^N$, together with its energy $J_{2N}$. An easy adaptation of [5, 6] shows that $\frac{J_{2N}}{2N}$ converges to $I_{per,\overline{R}} = I_{per}$. Moreover, the system $(\eta_N, \{Y_i^N\})$ is a test system for the minimization problem $I_{2N}$, hence

$$\frac{I_{2N}}{2N} \leq \frac{J_{2N}}{2N} \longrightarrow I_{per}.$$

This proves (3.2). We now show:

$$\lim_{N\to\infty} \frac{I_N}{N} \geq I_{per}. \tag{3.3}$$

In order to do so, we re-write the energy $I_N$: let $(\rho_N, \{X_i^N\})$ be a solution of $I_N$, and $\phi_N$ the associated effective potential (2.3). Then,

$$I_N = E^{TFW}(\rho_N, \{X_i^N\}) = \int_{\mathbf{R}} (\sqrt{\rho_N}\ ')^2 + \int_{\mathbf{R}} \rho_N^p + \frac{1}{2}\int_{\mathbf{R}} (\phi_N')^2,$$

according to the definition of $\phi_N$. Thus, we have:

$$\begin{aligned} I_N \;\; = \;\; & \int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\ ')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 + \int_{X_N^N}^{+\infty} (\sqrt{\rho_N}\ ')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \\ & + \sum_{i=1}^{N-1} \int_{X_i^N}^{X_{i+1}^N} (\sqrt{\rho_N}\ ')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2. \end{aligned}$$

First, we prove that for any $i \in \{1, \ldots, N-1\}$,

$$\int_{X_i^N}^{X_{i+1}^N} (\sqrt{\rho_N}\ ')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \geq I_{per}. \tag{3.4}$$

In order to do so, we introduce $Y_i^N$ as the unique point in $]X_i^N, X_{i+1}^N[$ such that $\phi_N'(Y_i^N) = 0$. It exists since $\phi_N'$ ranges monotonically from $-\frac{1}{2}$ to $\frac{1}{2}$ on $]X_i^N, X_{i+1}^N[$. We then consider the function $\rho_i$ defined by:

$$\rho_i(x) = \begin{cases} \rho_N(x) & \text{if} \quad X_i^N \leq x \leq Y_i^N, \\ \rho_N(X_i^N - x) & \text{if} \quad 2X_i^N - Y_i^N \leq x \leq X_i^N. \end{cases} \tag{3.5}$$

This defines a function $\rho_i$ on $[2X_i^N - Y_i^N, Y_i^N]$ satisfying periodic boundary conditions. We define $\phi_i$ in the same way, namely

$$\phi_i(x) = \begin{cases} \phi_N(x) & \text{if} \quad X_i^N \leq x \leq Y_i^N, \\ \phi_N(X_i^N - x) & \text{if} \quad 2X_i^N - Y_i^N \leq x \leq X_i^N, \end{cases} \tag{3.6}$$

and prolong these two functions by periodicity. Thanks to (2.5), one then easily finds that $-\phi_i{}'' = \delta_{X_i^N} - \rho_i$ on $[2X_i^N - Y_i^N, Y_i^N]$, together with periodic boundary conditions. This implies, from the definition of $G_{2(X_i^N - Y_i^N)}$ (1.7), that

$$\phi_i(x) = \left(G_{2(X_i^N-Y_i^N)} - \rho_i \star_{[-(Y_i^N - X_i^N), Y_i^N - X_i^N]} G_{2(X_i^N - Y_i^N)}\right)(x + X_i^N) + a,$$

where $a$ is a constant. Thus, the derivatives of these two effective potentials are equal, and

$$\begin{aligned}\int_{X_i^N}^{Y_i^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 &= \frac{1}{2}\int_{2X_i^N - Y_i^N}^{Y_i^N} (\sqrt{\rho_i}\,')^2 + \rho_i^p + \frac{1}{2}(\phi_i{}')^2 \\ &= \frac{1}{2} E_{per,R}^{TFW}(\rho_i) \geq \frac{1}{2} I_{per}. \qquad (3.7)\end{aligned}$$

A similar treatment may be done concerning the integral over $[Y_i^N, X_{i+1}^N]$, which proves (3.4).

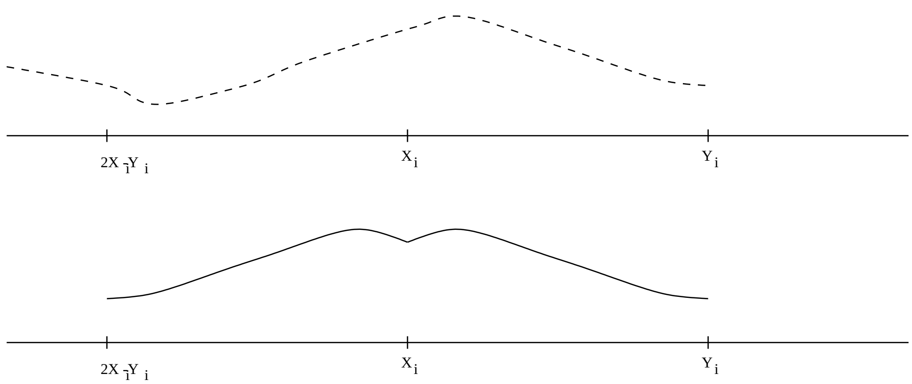


Figure 1: The symmetrisation process described by equations (3.5) and (3.6): above, the true density $\rho_N$, and below, the symmetrised one.

We then prove that $\displaystyle\int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \geq \frac{1}{2} I_1$. Consider the function $\rho_0$ defined by

$$\rho_0(x) = \begin{cases} \rho_N(x) & \text{if} \quad x \leq X_1^N, \\ \rho_N(X_1^N - x) & \text{if} \quad x > X_1^N. \end{cases}$$

Define $\phi_0$ in the same way from $\phi_N$. We then have $\phi_0'' = \delta_{X_1^N} - \rho_0$, and $\phi_0$ converges to some constant at infinity. This implies in particular that $\phi_0 = \phi_0^0 + a$, where $a \in \mathbf{R}$ and $\phi_0^0 = \frac{1}{2}\rho_1 \star |x| - \frac{1}{2}|x - X_1^N|$. As a consequence, $\phi_0{}' = \phi_0^{0\prime}$, hence

$$\begin{aligned}\int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 &= \frac{1}{2}\int_{\mathbf{R}} (\sqrt{\rho_1}\,')^2 + \rho_1^p + \frac{1}{2}(\phi_1^{0\prime})^2 \\ &= \frac{1}{2} E^{TFW}(\rho_1, X_1^N) \geq \frac{1}{2} I_1.\end{aligned}$$

Likewise, $\displaystyle\int_{X_N^N}^{+\infty}(\sqrt{\rho_N}\ ')^2+\rho_N^p+\frac{1}{2}(\phi_N')^2 \geq \frac{1}{2}I_1$. Together with (3.4), this shows that

$$I_N \geq (N-1)I_{per}+I_1.$$

Dividing this inequality by $N$ and letting $N$ go to infinity, we find (3.2). $\Diamond$

# 4 Convergence of the density

This section is devoted to the proof of Theorem 1.2.

We know from [3] that $I_1 > I_{per}$. We also know that, $I_{per,R}$ being defined by (1.8), $\lim\limits_{R\to\infty} I_{per,R} = I_1$. This implies in particular that there exists an $R_0 > 0$ such that

$$\forall R > R_0, \quad I_{per,R} > \frac{1}{2}(I_{per}+I_1). \tag{4.1}$$

**Remark 4.1** *Inequality (4.1) also shows that the set of solutions $\overline{R}$ of problem (1.9) is bounded from above.*

Next, we notice that inequality (3.7) may be improved, since $\frac{1}{2}E_{per,R}^{TFW}(\rho_i) \geq I_{per,R}$ is an equality only if $\rho_i$ is the solution of $I_{per,R}$, due to the strict convexity of this variational problem [2]. Thus, denoting by $A_N$ the number of indexes $i$ in $\{1,\dots,N\}$ such that $X_{i+1}^N - X_i^N > R_0$, we have:

$$I_N \geq \frac{A_N}{4}(I_1+I_{per}) + (N-\frac{A_N}{2}-1)I_{per}+I_1.$$

We thus have $\frac{I_N}{N} - I_{per} + \frac{I_{per}-I_1}{N} \geq \frac{I_1-I_{per}}{4}\frac{A_N}{N}$, which implies, according to Theorem 1.1 and the fact that $I_1 > I_{per}$, that

$$A_N = o(N), \quad \text{as} \quad N \longrightarrow \infty. \tag{4.2}$$

Next, denote by $B_N$ the number of indexes $i \in \{1,\dots,N\}$ such that

$$\liminf \int_{X_i^N}^{X_{i+1}^N}(\sqrt{\rho_N}\ ')^2+\rho_N^p+\frac{1}{2}(\phi_N')^2 > I_{per}.$$

For the same reason, $B_N$ also satisfies (4.2). Hence, one can find a sequence $(i_N)$ of indexes such that:

(i) $i_N \longrightarrow \infty, \quad N-i_N \longrightarrow \infty,$

(ii) $X_{i_N+1}^N - X_{i_N}^N \leq R_0,$

(iii) $\displaystyle\int_{X_{i_N}^N}^{X_{i_N+1}^N}(\sqrt{\rho_N}\ ')^2+\rho_N^p+\frac{1}{2}(\phi_N')^2 \longrightarrow I_{per}.$

Changing the origin if necessary, we may assume without loss of generality that $X_{i_N}^N = 0$. From (iii) and Corollary 2.3, we deduce that $\sqrt{\rho_N}$ is bounded in $H^1_{loc} \cap L^\infty$. Using (iii) and Proposition 2.4, similar bounds may be obtained for $\phi_N$. Hence, we may extract a subsequence so that $(\rho_N, \phi_N)$ converges to some $(\rho_\infty, \phi_\infty)$ strongly in all $L^p_{loc}$, and that $X^N_{i_N+1}$ converges to $R \leq R_0$. We may also assume that $Y^N_{i_N}$ converges to some $r \leq R$. As a consequence, we have:

$$\int_0^R (\sqrt{\rho_\infty}\ ')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \leq I_{per}. \tag{4.3}$$

Moreover, equation $\phi_N'' = \rho_N$ passes to the limit, together with the fact that $\phi_N'(0) = -\frac{1}{2} = -\phi_N'(X^N_{i_N+1})$ and $\phi_N'(Y^N_{i_N}) = 0$, so that $\phi_\infty'(0) = -\phi_\infty'(R) = -\frac{1}{2}$, and $\phi_\infty'(r) = 0$. Hence, using the same tricks as in the proof of Theorem 1.1, we have:

$$\int_0^r (\sqrt{\rho_\infty}\ ')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \geq \frac{1}{2} I_{per}, \tag{4.4}$$

$$\int_r^R (\sqrt{\rho_\infty}\ ')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \geq \frac{1}{2} I_{per}, \tag{4.5}$$

and equality holds in (4.4), respectively (4.5), only if $\rho_\infty$ is the solution $\rho_{per,2r}$ of the periodic problem $I_{per,2r}$, respectively the solution $\rho_{per,2(R-r)}$ of $I_{per,2(R-r)}$. On the other hand, (4.3) implies that equality does hold in these two equations, showing that $\rho_\infty = \rho_{per,2r}$ on $[0,r]$ and $\rho_\infty = \rho_{per,2(R-r)}$ on $[r,R]$. Hence, setting $u_\infty = \sqrt{\rho_\infty}$, the functions $(u_\infty, \phi_\infty)$ are solutions of the system (2.4) on $]0,R[$, namely

$$\begin{cases} -u_\infty'' + p u_\infty^{2p-1} - \phi_\infty u_\infty = 0, \\ -\phi_\infty'' = -u_\infty^2. \end{cases} \tag{4.6}$$

Consequently, $\phi_\infty = \phi_{per,2r}$ on $[0,r]$, where $\phi_{per,2r} = G_{2r} - G_{2r} \star \rho_{per,2r}$. Hence, $(u_\infty, \phi_\infty)$ and $(\sqrt{\rho_{per,2r}}, \phi_{per,2r})$ share the same values and the same derivatives at 0, and satisfy the same differential equation on $]0,R[$. According to Cauchy-Lipschitz theorem, together with the fact that the function $(u,\phi) \mapsto (pu^{2p-1} - \phi u, -u^2)$ is locally lipschitz continuous from $\mathbf{R}^2$ to $\mathbf{R}^2$, this implies that they are equal on the whole interval $[0,R]$. Since the unique point at which $\phi'_{per,2r}$ reaches $\frac{1}{2}$ is $2r$, this implies that $R = 2r$ is a solution of problem $I_{per}$, and that $\rho_\infty = \rho_{per,R}$. Next, we point out that (4.6) is also satisfied on the right of $R$, so that, still using Cauchy-Lipschitz theorem, $(\rho_\infty, \phi_\infty) = (\rho_{per,R}, \phi_{per,R})$ on the right of $R$. Hence, the unique point satisfying $\phi_\infty' = \frac{1}{2}$ on the right of $R$ is $2R$, which means that $X^N_{i_N+2} \longrightarrow 2R$ as $N$ goes to infinity. Carrying on this process on both sides of the interval $[0,R]$, we conclude our proof. $\diamondsuit$

# 5 Consequences and extensions

We give in this section some side-remarks and extension to the Thomas-Fermi (TF) case. First of all, an adaptation of the above proof shows that:

**Corollary 5.1** *(a) Let $\{X_i\}_{i\in\mathbf{Z}}$ be a periodic configuration of nuclei, in the sense that $X_{i+N} = X_i + L$, for some fixed $N, L$. Then the minimum of energy per nuclei, as defined in (5.1) below, is reached only for the equidistant configuration ($X_{i+1} = X_i + \frac{L}{N}$).*

*(b) Let $(\rho, \{X_i\})$ be a system such that $0 < X_1 \leq X_2 \leq \cdots \leq X_N < L$, and $\rho$ satisfies periodic boundary conditions on $]0, L[$. Assume in addition that this system is a minimizer of the following energy:*

$$\overline{E}_L^{TFW}(\rho, \{X_i\}) = \int_0^L (\sqrt{\rho}\,')^2 + \int_0^L \rho^p + \frac{1}{2}\int_0^L (\phi')^2,$$

*where $\phi$ is a solution of $-\phi'' = \sum \delta_{X_i} - \rho$ with periodic boundary conditions. Then $X_{i+1} = X_i + \frac{L}{N}$, for all $i$.*

In (a), the periodic TFW energy is defined by (we assume that $X_0 = 0$):

$$\begin{aligned} \tilde{E}^{TFW}(\rho, \{X_i\}) &= \int_{-\frac{L}{2}}^{\frac{L}{2}} (\sqrt{\rho}\,')^2 + \int_{-\frac{L}{2}}^{\frac{L}{2}} \rho^p - \sum_{|j| < \frac{N}{2}} \int_{-\frac{L}{2}}^{\frac{L}{2}} G_L(x - X_j)\rho(x)dx \\ &\quad + \frac{1}{2}\int_{-\frac{L}{2}}^{\frac{L}{2}}\int_{-\frac{L}{2}}^{\frac{L}{2}} \rho(x)G_L(x-y)\rho(y)dxdy + \frac{1}{2}\sum_{|i|,|j|<\frac{N}{2}} G_L(X_i - X_j), \end{aligned}$$

where $G_L$ is defined by (1.7), and the electronic ground state is:

$$I_{per,L}^N = \inf\left\{ \tilde{E}^{TFW}(\rho, \{X_i\}), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0, L[), \quad \int_0^L \rho = N \right\}, \tag{5.1}$$

and the energy per nuclei is equal to $\frac{I_{per,L}^N}{N}$.

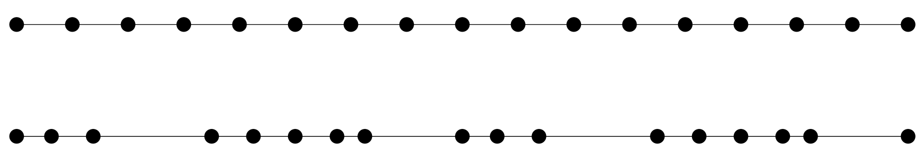

Figure 2: Two periodic distributions of nuclei, with $N = 9$. Corollary 5.1 states that the above one has strictly lower energy than the other.

Using similar techniques as for the TFW case, one can show that Corollary 5.1 holds in the TF case, where one forgets the term $\int (\sqrt{\rho}\,')^2$ in the energy. On the contrary, Theorem 1.2 does not hold in this case since problem (1.1) has no solution [9]. More precisely, $I_N = NI_1$ in this case, and this value is reached only in the limit $X_{i+1} - X_i \to \infty$, for all $i$. The proof is more simple in fact, since (2.1) is still valid, and (2.4) reads:

$$\begin{cases} -\phi'' + \left(\frac{1}{p}\right)^{\frac{1}{p-1}} \phi^{\frac{1}{p-1}} = \sum_{i=1}^N \delta_{X_i}, \\ \phi = p\rho^{p-1}. \end{cases}$$

And the analogue of (2.6) is $-\frac{1}{2}\phi'^2 + (p-1)\left(\frac{1}{p}\phi\right)^{\frac{p}{p-1}} = a$, where $a$ is a constant (not necessarily 0). Hence, thanks to the fact that $\phi'^2$ has a fixed value at $X_i$, so does $\phi$, and we may apply Cauchy-Lipschitz theorem to show that the configuration is indeed periodic with one atom per cell.

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