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On the crystal ground state in the Schrödinger–Poisson model with point ions

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Abstract—A space-periodic ground state is shown to exist for lattices of point ions in $\mathbb{R}^3$ coupled to the Schrödinger and scalar fields. The coupling requires renormalization due to the singularity of the Coulomb self-action. The ground state is constructed by minimizing the renormalized energy per cell. This energy is bounded from below when the charge of each ion is positive. The elementary cell is necessarily neutral.

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KEY WORDS: *crystal*; *lattice*; *ion*; *charge*; *wave function*; *potential*; *Schrödinger equation*; *Poisson equation*; *renormalization*; *elementary cell*; *energy per cell*; *Coulomb energy*; *minimization*; *neutrality condition*; *spectrum*; *embedding theorems*; *Fourier transform*; *infrared divergence*; *variation*

1. INTRODUCTION

We consider 3-dimensional crystal lattices in $\mathbb{R}^3$,

$$\Gamma := \{x(n) = a_1 n_1 + a_2 n_2 + a_3 n_3 : n = (n_1, n_2, n_3) \in \mathbb{Z}^3\}, \qquad (1.1) \quad \{\texttt{Ga3}\}$$

$a_l \in \mathbb{R}^3$ are linearly independent periods. Born and Oppenheimer [1] developed the quantum dynamical approach to the crystal structure, separating the motion of "light electrons" and of "heavy ions". As an extreme form of this separation, the ions could be considered as classical nonrelativistic particles governed by the Lorentz equations neglecting the magnetic field, while the electrons could be described by the Schrödinger equation neglecting the electron spin. The scalar potential is the solution to the corresponding Poisson equation.

We consider a crystal with N ions per cell. Let $\sigma_j(y) = |e|Z_j\delta(y)$ be the charge density and $M_j > 0$ be the mass of the corresponding ion, $j = 1, \dots, N$. Then the coupled equations read

$$i\hbar\dot\psi(x,t) = -\frac{\hbar^2}{2\mathrm{m}}\Delta\psi(x,t) + e\phi(x,t)\psi(x,t), \quad x \in \mathbb{R}^3, \qquad (1.2) \quad \{\texttt{LPS1}\}$$

$$-\Delta\phi(x,t) = \rho(x,t) := \sum_{j=1}^{N}\sum_{n\in\mathbb{Z}^3}\sigma_j(x - x(n) - q_j(n,t)) + e|\psi(x,t)|^2, \quad x \in \mathbb{R}^3, \qquad (1.3) \quad \{\texttt{LPS2}\}$$

$$M_j\ddot q_j(n,t) = -|e|Z_j\nabla\phi_{nj}(x(n) + q_j(n,t)), \quad n \in \mathbb{Z}^3, \quad j = 1, \dots, N. \qquad (1.4) \quad \{\texttt{LPS}\}$$

Here, $e < 0$ is the electron charge, m is its mass, $\psi(x,t)$ denotes the wave function of the electron field, and $\phi(x,t)$ is the potential of the scalar field generated by the ions and the electrons. Further, $(\cdot,\cdot)$ stands for the Hermitian scalar product in the Hilbert space $L^2(\mathbb{R}^3)$, and

$$\nabla\phi_{nj}(x(n) + q_j(n,t)) := \nabla_y\left[\phi(x(n) + q_j(n,t) + y) - \frac{|e|Z_j}{4\pi|y|}\right]\Bigg|_{y=0}. \qquad (1.5) \quad \{\texttt{phinj}\}$$

All the derivatives here and below will be understood in the sense of distributions. The system is nonlinear and translation invariant; i.e., $\psi(x-a,t)$, $\phi(x-a,t)$, $q_j(n,t)+a$ is also a solution for any $a\in\mathbb{R}^3$.

A dynamical quantum description of the solid state as a many-body system gas not yet been rigorously established (see the introduction of [2] and the preface of [3]). Up-to-date rigorous results are concerned only with the ground state in different models (see below).

The classical Bethe–Sommerfeld's "one-electron" theory, which depends on periodic Schrödinger equation, does not take into account the oscillations of ions. Moreover, the choice of a periodic potential in this theory is very problematic and corresponds to the fixation of ion positions (which are unknown).

System (1.2)–(1.4) eliminates these difficulties. However, it does not respect the electron spin like the periodic Schrödinger equation. To circumvent this deficiency one should replace the Schrödinger equation by the Hartree–Fock equations as the next step towards a more realistic model. However, we expect that the techniques developed for system (1.2)–(1.4) will be also useful for more realistic dynamical models of crystals. These goals were our main motivation in writing this paper.

Here, we make the first step at proving the existence of the ground state, which is a Γ-periodic stationary solution $\psi^0(x)e^{-i\omega^0 t}$, $\phi^0(x)$, $\overline{q}=(q_1^0,\dots,q_N^0)$ to system (1.2)–(1.4):

$$\hbar\omega^0\psi^0(x)=-\frac{\hbar^2}{2\mathrm{m}}\Delta\psi^0(x)+e\phi^0(x)\psi^0(x),\qquad x\in T^3, \tag{1.6}$$ {LPS3}

$$-\Delta\phi^0(x)=\rho^0(x):=\sigma^0(x)+e|\psi^0(x)|^2,\qquad x\in T^3, \tag{1.7}$$ {LPS4}

$$0=-|e|Z_j\nabla\phi^0_{nj}(q_j^0),\qquad j=1,\dots,N. \tag{1.8}$$ {LPS3g}

Here, $T^3:=\mathbb{R}^3/\Gamma$ denotes the ‘elementary cell" of the crystal, $\langle\cdot,\cdot\rangle$ stands for the Hermitian scalar product in the complex Hilbert space $L^2(T^3)$ and its different extensions, and

$$\sigma^0(x):=\sum_{j=1}^N\sigma_j(x-q_j^0),\qquad \sigma_j(y):=|e|Z_j\delta(y). \tag{1.9}$$ {rrr}

The right-hand side of (1.8) is defined similarly to (1.5):

$$\nabla\phi^0_{nj}(q_j^0):=\nabla_y\left[\phi(q_j^0+y)-\frac{|e|Z_j}{4\pi|y|}\right]\Bigg|_{y=0} \tag{1.10}$$ {phinj0}

Similarly to (1.2)–(1.4), system (1.6)–(1.8) is translation invariant. Note that ω^0 must be real, because $\operatorname{Im}\omega^0\neq 0$ means the instability of the ground state: a decay as $t\to\infty$ if $\operatorname{Im}\omega^0<0$ and an explosion if $\operatorname{Im}\omega^0>0$. We have

$$\int_{T^3}\sigma^0(x)\,dx=Z|e|,\qquad Z:=\sum_j Z_j. \tag{1.11}$$ {intro}

The total charge per cell should be zero (cf. [4]):

$$\int_{T^3}\rho^0(x)\,dx=\int_{T^3}[\sigma^0(x)+e|\psi^0(x)|^2]\,dx=0. \tag{1.12}$$ {neu10}

This neutrality condition follows directly from equation (1.7) by integration and using the Γ-periodicity of $\phi^0(x)$. Equivalently, the neutrality condition can be written as the normalization

$$\int_{T^3}|\psi^0(x)|^2\,dx=Z. \tag{1.13}$$ {neuZ}

Our main condition is the following:

$$\textbf{Positivity condition:} \qquad Z_j > 0, \quad j = 1, \dots, N. \tag{1.14}$$ {Zp}

Let us comment on our approach. The neutrality condition (1.13) defines the submanifold $\mathcal{M}$ in the space $H^1(T^3) \times (T^3)^N$ of space-periodic configurations $(\psi^0, \overline{q}^0)$. We construct a ground state as a minimizer over $\mathcal{M}$ of the energy per cell (2.3). Previously, we have established similar results [**?**] for crystals with 1D, 2D and 3D lattices of smeared ions in $\mathbb{R}^3$.

Our main novelties in the present paper are as follows.

I. We extend our results [**?**]to the point ions subtracting the infinite self-action in the renormalized equations.

II. We renormalize the energy per cell subtracting the infinite Coulomb self-action of the point ions.

III. We put forward a bound from below for the renormalized energy under the assumption (1.14).

The minimization strategy ensures the existence of a ground state for any lattice (1.1). One could expect that a stable lattice should provide a local minimum of the energy per cell for fixed N and Z_j, but this is still an open problem.

Some comment on related works are worth making. For atomic systems in $\mathbb{R}^3$, a ground state was constructed by Lieb, Simon and P. Lions in the case of the Hartree and Hartree–Fock models [5],[6], [7], and by Nier for the Schrödinger–Poisson model [8]. The Hartree–Fock dynamics for molecular systems in $\mathbb{R}^3$ was constructed by Cancès and Le Bris [9].

A mathematical theory of the stability of matter emerges from the pioneering works of Dyson, Lebowitz, Lenard, Lieb and others for the Schrödinger many-body model [10], [11], [12], [13]; see the survey in [14]. Recently, the theory was extended to the setting of quantized Maxwell field [15].

These results and methods were developed in the last two decades by Blanc, Le Bris, Catto, P. Lions and others to justify the thermodynamic limit for the Thomas–Fermi and Hartree–Fock models with space-periodic ion arrangement [16],[17],[18],[19] and to construct the corresponding space-periodic ground states [20], see the survey and further references in [21].

Recently, Giuliani, Lebowitz and Lieb have established the periodicity of the thermodynamic limit in the 1D local mean field model without the assumption of periodicity of the ion arrangement [22].

The paper is organized as follows. In Section 2, we renormalize the energy per cell and prove that the renormalized energy is bounded from below. In Section 3, we prove the compactness of the minimizing sequence, and in Section 4 calculate the energy variation. In the final Section 5, we prove the Schrödinger equation.

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2. THE RENORMALIZED ENERGY PER CELL

We consider system (1.6), (1.7) for the corresponding functions on the torus $T^3 = \mathbb{R}^3/\Gamma$ and for $q_{0j} \bmod \Gamma \in T^3$. For $s \in \mathbb{R}$, we denote by H^s the Sobolev space on the torus T^3, and for $1 \le p \le \infty$, we denote by L^p the Lebesgue space of functions on T^3.

The ground state will be constructed by minimizing the energy in the cell T^3. To this aim, we will minimize the energy with respect to $\overline{q} := (q_1, \dots, q_N) \in (T^3)^N$ and $\psi \in H^1$ satisfying the neutrality condition (1.12),

$$\int_{T^3} \rho(x)\, dx = 0, \qquad \rho(x) := \sigma(x) + \nu(x), \tag{2.1}$$ {neu1}

where we set

$$\sigma(x) := \sum_j \sigma_j(x-q_j), \qquad \nu(x) := e|\psi(x)|^2 \tag{2.2}$$ {rrr2}

similarly to (1.9). Let us note that the charge densities σ and ρ are finite Borel measures on T^3 for $\psi \in H^1$, since $\psi \in L^6$ by the Sobolev embedding theorem.

For sufficiently smooth (smeared) ion densities $\sigma(x)$ the energy in the periodic cell is defined as in [23],

$$E(\psi,\overline{q}) := \frac{\hbar^2}{2\mathrm{m}}\langle\nabla\psi(x),\nabla\psi(x)\rangle + \frac{1}{2}\langle\phi,\rho\rangle, \qquad \phi := Q\rho, \tag{2.3}$$ {HamsT}

where $\langle\cdot,\cdot\rangle$ is the Hermitian scalar product in L^2, and $Q\rho := (-\Delta)^{-1}\rho$ is well-defined by (2.1). Namely, consider the dual lattice

$$\Gamma^* = \{k(n) = b_1n_1 + b_2n_2 + b_3n_3 : n = (n_1,n_2,n_3) \in \mathbb{Z}^3\}, \tag{2.4}$$ {Ga3d}

where $b_l a_{k'} = 2\pi\delta_{kk'}$. Every finite measure ρ on T^3 admits the Fourier representation

$$\rho(x) = \frac{1}{\sqrt{|T^3|}}\sum_{k\in\Gamma^*}\hat\rho(k)e^{-ikx}, \qquad \hat\rho(k) = \frac{1}{\sqrt{|T^3|}}\int_{T^3} e^{ikx}\rho(x)\,dx, \tag{2.5}$$ {Fou}

where the Fourier coefficients $\hat\rho(k)$ are bounded. Respectively, we define the Coulomb potential

$$\phi(x) = Q\rho(x) := \frac{1}{\sqrt{|T^3|}}\sum_{k\in\Gamma^*\setminus 0}\frac{\hat\rho(k)}{k^2}e^{-ikx}. \tag{2.6}$$ {Fou2}

The function ϕ lies in L^2 and satisfies the Poisson equation $-\Delta\phi = \rho$, since $\hat\rho(0) = 0$ due to the neutrality condition (2.1). Finally,

$$\int_{T^3}\phi(x)\,dx = 0. \tag{2.7}$$ {Fou3}

For the smeared ions the energy (2.3) can be rewritten as

$$E(\psi,\overline{q}) = \frac{\hbar^2}{2\mathrm{m}}\langle\nabla\psi,\nabla\psi\rangle + \frac{1}{2}\langle Q\sigma,\sigma\rangle + \langle Q\sigma,\nu\rangle + \frac{1}{2}\langle Q\nu,\nu\rangle. \tag{2.8}$$ {HamsTf}

Let us show that for the point ions the Coulomb self-action energy

$$\langle Q\sigma,\sigma\rangle = \sum_{j,l=1}^{N}\langle Q\sigma_j,\sigma_l\rangle$$

is infinite. Namely, according to (2.6), the Coulomb potential of the ions reads as

$$\phi_{\rm ion}(x) := Q\sigma(x) = \frac{1}{\sqrt{|T^3|}}\sum_{k\in\Gamma^*\setminus 0}\frac{\hat\sigma(k)}{k^2}, \qquad \hat\sigma(k) = \frac{|e|}{\sqrt{|T^3|}}\sum_j Z_j e^{ikq_j}. \tag{2.9}$$ {Fou2n}

Hence, for the point ions,

$$\phi_{\rm ion}(x)=\sum_j\phi_j(x),\ \ \phi_j(x:=Q\sigma_j(x-q_j)=|e|Z_jG(x-q_j),\ \ G(x)=\sum_{k\in\Gamma^*\setminus 0}\frac{e^{-ikx}}{k^2}, \tag{2.10}$$ {Fou2h}

where $G(x)$ is the Green function introduced in [18]. Obviously, $\displaystyle\int_{T^3} G(x)\,dx = 0$ and $-\Delta G(x) = \delta(x)$. Therefore, by the elliptic regularity,

$$G \in C^\infty(T^3 \setminus 0), \qquad D(x) := G(x) - \frac{1}{4\pi|x|} \in C^\infty(|x| < \varepsilon) \tag{2.11}$$ {G}

for sufficiently small $\varepsilon > 0$. As a result, the self-action terms $\langle Q\sigma_j(x-q_j), \sigma_j(x-q_j)\rangle = |e|^2 Z_j^2 G(0)$ are infinite, while $\langle Q\sigma_j(x-q_j), \sigma_l(x-q_l)\rangle = |e|^2 Z_j Z_l G(q_j - q_l)$ are finite for $j \neq l$.

{rD0}

Remark 2.1. Let us note that $G(x)$ is symmetric with respect to the reflection $x \mapsto -x$ of the torus T^3. Therefore, the difference $D(x)$ is symmetric in the ball $|x| < \varepsilon$ with respect to this reflection, and hence

$$\nabla D(0) = 0. \tag{2.12}$$ {G0}

From now on we consider the point ions (1.9); the energy (2.8) will be renormalized by subtracting the infinite self-action terms:

$$E_r(\psi, \overline{q}) = \frac{\hbar^2}{2\mathrm{m}}\langle \nabla\psi, \nabla\psi\rangle + \frac{1}{2}\sum_{j\neq l}\langle Q\sigma_j(x-q_j), \sigma_l(x-q_l)\rangle + \langle Q\sigma, \nu\rangle + \frac{1}{2}\langle Q\nu, \nu\rangle. \tag{2.13}$$ {HamsTr}

Note that $\nu \in L^2$ for $\psi \in H^1$ by the Sobolev embedding theorem, and besides $Q\sigma \in L^2$. Hence, the renormalized energy is finite for $\psi \in H^1$. Next step is to check that the renormalized energy is bounded from below. We set

$$\mathcal{X} := \{\overline{q} \in (T^3)^N : q_j \neq q_l \ \text{ for } \ j \neq l\}, \qquad d(\overline{q}) := \min_{j\neq l} \operatorname{dist}(q_j, q_l). \tag{2.14}$$ {cX}

Definition 2.2. We set $\mathcal{M} := M \times \mathcal{X}$, where M denotes the manifold (cf. (1.13))

$$M = \Big\{\psi \in H^1 : \int_{T^3} |\psi(x)|^2\,dx = Z\Big\} \tag{2.15}$$ {MZ}

endowed with the topology of $H^1 \times \mathcal{X}$.

{lf}

Lemma 2.3. *Let condition* (1.14) *hold. Then the functional E_r is continuous on $\mathcal{M}$, and the bound holds*

$$E_r(\psi, \overline{q}) \geq \varepsilon\|\psi\|_{H^1}^2 + \frac{q}{d(\overline{q})} + \frac{1}{2}\langle Q\nu, \nu\rangle - C, \qquad (\psi, \overline{q}) \in \mathcal{M}, \tag{2.16}$$ {HamsTr2}

where $q, \varepsilon > 0$.

Proof. First, $\nu := e|\psi(x)|^2 \in L^2$, since $\|\nu\|_{L^2} = e^2\|\psi\|_{L^4}^2 \leq C_1\|\psi\|_{H^1}^2$ by the Sobolev embedding theorem [24], [25]. Further, $Q\sigma \in L^2$, since σ is a finite Borel measure on T^3 by (2.2). Hence, for any $\delta > 0$,

$$|\langle Q\sigma(x), \nu(x)\rangle| \leq C\|\psi\|_{L^4}^2 \leq \delta\|\psi\|_{L^6}^2 + C(\delta)\|\psi\|_{L^2}^2 \leq C_2\delta\|\psi\|_{H^1}^2 + C(\delta)Z. \tag{2.17}$$ {f}

Here, the second inequality follows in view of the Young inequality from the inequality $\|\psi\|_{L^4} \leq \|\psi\|_{L^6}^{3/4}\|\psi\|_{L^2}^{1/4}$, which holds by the M. Riesz convexity theorem. This theorem can be derived using the Hölder inequality, but in our case the Cauchy–Schwarz inequality is sufficient:

$$\int |\psi(x)|^3|\psi(x)|\,dx \leq [\int |\psi(x)|^6\,dx]^{1/2}[\int |\psi(x)|^2\,dx]^{1/2}.$$

Therefore, the functional $(\psi, \overline{q}) \mapsto \langle Q\sigma, \nu\rangle$ is continuous on $\mathcal{M}$ in the topology of $H^1 \times \mathcal{X}$.

On the other hand, $\|\psi\|_{H^1}^2 = \displaystyle\int_{T^3} |\nabla\psi(x)|^2\,dx + Z$ for $\psi \in M$. Hence, the bound (2.16) follows if we take $C_2\delta < \hbar^2/(2\mathrm{m})$. ■

3. COMPACTNESS OF A MINIMIZING SEQUENCE

The energy is finite and bounded from below on the manifold $\mathcal{M}$ by Lemma 2.3. Hence, there exists a minimizing sequence $(\psi_n, \overline{q}_n) \in \mathcal{M}$ such that

$$E_r(\psi_n, \overline{q}_n) \to E_r^0 := \inf_{\mathcal{M}} E(\psi, \overline{q}), \qquad n \to \infty. \tag{3.1}$$ {min}

Remark 3.1. For sufficiently smooth charge densities σ_j the energy (2.8) is also finite, and its difference from (2.13) is $\sum \langle Q\sigma_j(x - q_j), \sigma_j(x - q_j)\rangle = \sum \langle Q\sigma_j, \sigma_j\rangle$ up to the constant factor $1/2$. This difference does not depend on ψ and $\overline{q}$. Hence, the corresponding minimizers coincide.

Our main result is the following

{t3}

Theorem 3.2. i) *There exists* $(\psi^0, \overline{q}^0) \in \mathcal{M}$ *such that*

$$E_r(\psi^0, \overline{q}^0) = E_r^0. \tag{3.2}$$ {U0min}

ii) *Moreover,* ψ^0 *satisfies equations* (1.6)–(1.8) *with a real potential* $\phi^0 \in L^2$ *and* $\omega^0 \in \mathbb{R}$.

To prove i) we set

$$\rho_n(x) := \sigma_n(x) + e|\psi_n(x)|^2, \quad \sigma_n(x) := \sum_j \mu_j^{\rm per}(x - q_{nj}), \quad \nu_n(x) := e|\psi_n(x)|^2. \tag{3.3}$$ {ron}

The sequence ψ_n is bounded in H^1 by (3.1) and (2.16), and hence the corresponding sequence ν_n is bounded in L^2 by the Sobolev embedding theorem [24], [25]. Respectively, the corresponding sequences $Q\sigma_n$ and $\phi_n := Q\rho_n$ are bounded in L^2.

Hence, the sequence ψ_n is precompact in L^p for any $p \in [1, 6)$ by the Sobolev embedding theorem. As a result, there exist a subsequence $n' \to \infty$ for which

$$\psi_{n'} \xrightarrow{L^p} \psi^0, \quad \nu_{n'}(x) \xrightarrow{L^2} \nu^0, \quad \phi_{n'} \xrightharpoonup{L^2_w} \phi^0, \quad \overline{q}_{n'} \to \overline{q}^0 \in \mathcal{X}, \qquad n' \to \infty \tag{3.4}$$ {subs}

with any $p \in [1, 6)$. Respectively, the convergences

$$\sigma_{n'} \to \sigma^0, \qquad \rho_{n'} \to \rho^0, \qquad n' \to \infty. \tag{3.5}$$ {subs1}

hold in the sense of distributions, where $\sigma^0(x)$ and $\rho^0(x)$ are defined by (1.9) and (1.7). Therefore,

$$Q\sigma_{n'} \xrightharpoonup{L^2_w} Q\sigma^0, \qquad n' \to \infty. \tag{3.6}$$ {3subs2}

Hence, the neutrality condition (1.12) holds, $(\psi^0, \overline{q}^0) \in \mathcal{M}$, $\phi^0 \in L^2$, and for these limit functions we have

$$-\Delta\phi^0 = \rho^0, \qquad \int_{T^3} \phi^0(x)\, dx = 0. \tag{3.7}$$ {phi0}

To prove identity (3.2), we write the energy (2.13) as the sum $E_r = E_1 + E_2 + E_3 + E_4$, where

$$E_1(\psi, \overline{q}) = \frac{\hbar^2}{2\mathrm{m}} \langle \nabla\psi(x), \nabla\psi(x)\rangle, \qquad E_2(\psi, \overline{q}) = \frac{1}{2} \sum_{j \neq l} \langle Q\sigma(x - q_j), \sigma(x - q_l)\rangle,$$

$$E_3(\psi, \overline{q}) = \langle Q\sigma(x), \nu(x)\rangle, \qquad E_4(\psi, \overline{q}) = \frac{1}{2} \langle Q\nu(x), \nu(x)\rangle.$$

Finally, the convergences (3.4) and (3.6) imply that

$$E_1(\psi^0, \overline{q}^0) \le \liminf_{n' \to \infty} E_1(\psi_{n'}, \overline{q}_{n'}), \qquad E_l(\psi^0, \overline{q}^0) = \lim_{n' \to \infty} E_l(\psi_{n'}, \overline{q}_{n'}), \quad l = 2, 3, 4.$$

These limits, together with (3.1), give that $E_r(\psi^0, \overline{q}^0) \le E_r^0$. Now (3.2) follows from the definition of E_r^0, since $(\psi^0, \overline{q}^0) \in \mathcal{M}$. This proves assertion i) of Theorem 3.2.

We will prove assertion ii) of Theorem 3.2 in next sections.

4. VARIATION OF THE ENERGY

Assertion ii) of Theorem 3.2 follows from next result.

{tgs23}

Proposition 4.1. *The limit functions* (3.4) *satisfy equations* (1.6)–(1.8) *with* $\omega^0 \in \mathbb{R}$.

The Poisson equation (1.7) is proved in (3.7). The Lorentz equation (1.8) follows by differentiation of the energy (2.13) in q_j. Namely, the derivative at the minimal point $(\psi^0, \overline{q}^0)$ should vanish: taking into account (2.10), we obtain

$$0 = \nabla_{q_j} E_r(\psi^0, \overline{q}^0) = \sum_{k \neq j} \langle Q\nabla\sigma_j(x - q_j^0), \sigma_l(x - q_l^0)\rangle + \langle Q\nabla\sigma_j(x - q_j^0), \nu^0\rangle$$
$$= \langle \nabla\sigma_j(x - q_j^0), \phi^0(x) - \phi_j^0(x)\rangle = -\langle \sigma_j(x - q_j^0), \nabla[\phi^0(x) - \phi_j^0(x)]\rangle,$$

where $\phi_j^0(x) := Q\sigma_j(x - q_j^0)$ as in (2.10). Finally, the last expression coincides with the right-hand side of (1.8) by its definition (1.10) and in view of (2.12).

It remains to prove the Schrödinger equation (1.6). Let us denote $\mathcal{E}_r(\psi) := E_r(\psi, \overline{q}^0)$. We derive (1.6) in next sections, equating the variation of $\mathcal{E}_r(\cdot)|_M$ to zero at $\psi = \psi^0$. In this section we calculate the corresponding Gâteaux variational derivative.

We should work directly on M introducing an atlas in a neighborhood of ψ^0 in M.Let us define the atlas as the stereographic projection from the tangent plane $TM(\psi^0) = (\psi^0)^\perp := \{\psi \in H^1 : \langle\psi, \psi^0\rangle = 0\}$ to the sphere (2.15):

$$\psi_\tau = \frac{\psi^0 + \tau}{\|\psi^0 + \tau\|_{L^2}}\sqrt{Z}, \qquad \tau \in (\psi^0)^\perp. \tag{4.1}$$ {3atlas}

Obviously,

$$\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \psi_{\varepsilon\tau} = \tau, \qquad \tau \in (\psi^0)^\perp, \tag{4.2}$$ {3tau}

where the derivative exists in H^1. We define the "Gâteaux derivative" of $\mathcal{E}_r(\cdot)|_M$ as

$$D_\tau \mathcal{E}_r(\psi^0) := \lim_{\varepsilon\to 0} \frac{\mathcal{E}_r(\psi_{\varepsilon\tau}) - \mathcal{E}_r(\psi^0)}{\varepsilon} \tag{4.3}$$ {3Gder}

if this limit exists. We should however restrict the set of allowed tangent vectors τ.

Definition 4.2. $\mathcal{C}^0$ is the space of test functions $\tau \in (\psi^0)^\perp \cap C^\infty(T^3)$.

Obviously, $\mathcal{C}^0$ is dense in $(\psi^0)^\perp$ in the norm of H^1.

{3lvar}

Lemma 4.3. *Let* $\tau \in \mathcal{C}^0$. *Then the derivative* (4.3) *exists and*

$$D_\tau \mathcal{E}_r(\psi^0) = \int_{T^3} \Big[\frac{\hbar^2}{2\mathrm{m}}(\nabla\tau\overline{\nabla\psi^0} + \nabla\psi^0\overline{\nabla\tau}) + eQ\rho^0(\tau\overline{\psi^0} + \psi^0\overline{\tau})\Big]\,dx. \tag{4.4}$$ {3Gder2}

Proof. Let us denote $\nu_{\varepsilon\tau}(x) := e|\psi_{\varepsilon\tau}(x)|^2$. Then it suffices to prove the following lemma.

{3lL2}

Lemma 4.4. *For* $\tau \in \mathcal{C}^0$ *we have* $\nu_{\varepsilon\tau} \in L^2$ *and*

$$D_\tau \nu := \lim_{\varepsilon\to 0} \frac{\nu_{\varepsilon\tau} - \nu_0}{\varepsilon} = e(\tau\overline{\psi^0} + \psi^0\overline{\tau}), \tag{4.5}$$ {3Gder3}

where the limit holds in L^2.

Proof. In the polar coordinates

$$\psi_{\varepsilon\tau}=(\psi^0+\varepsilon\tau)\cos\alpha,\qquad \alpha=\alpha(\varepsilon)=\arctan\frac{\varepsilon\|\tau\|_{L^2}}{\|\psi^0\|_{L^2}}. \qquad (4.6) \quad \{3al\}$$

Hence,

$$\nu_{\varepsilon\tau}=e\cos^2\alpha|\psi^0+\varepsilon\tau|^2=\nu^0+e\varepsilon\cos^2\alpha(\tau\overline{\psi^0}+\psi^0\overline{\tau})+e[\varepsilon^2|\tau|^2\cos^2\alpha-|\psi^0|^2\sin^2\alpha]. \qquad (4.7) \quad \{3rod\}$$

It remains to estimate the last term of (4.7),

$$R_\varepsilon:=\Lambda[\varepsilon^2|\tau|^2\cos^2\alpha-|\psi^0|^2\sin^2\alpha]. \qquad (4.8) \quad \{3lt\}$$

Here, $|\psi^0|^2\in L^2$, since $\psi^0\in H^1\subset L^6$. Finally, $|\tau|^2\in L^2$ and $\sin^2\alpha\sim\varepsilon^2$. Hence, the convergence (4.5) holds in L^2. ■

Now (4.4) follows by differentiation in ε of (2.13) with $\psi=\psi_{\varepsilon\tau}$, $\sigma=\sigma^0$ and $\nu=\nu_{\varepsilon\tau}$. ■

5. THE SCHRÖDINGER EQUATION

Since ψ^0 is a minimal point, the Gâteaux derivative (4.4) vanishes, and so

$$\int_{T_2}\Big[\frac{\hbar^2}{2\mathrm{m}}(\nabla\tau\overline{\nabla\psi^0}+\nabla\psi^0\overline{\nabla\tau})+eQ\rho^0(\tau\overline{\psi^0}+\psi^0\overline{\tau})\Big]\,dx=0. \qquad (5.1) \quad \{3GaD\}$$

Substituting $i\tau$ instead of τ in this identity and subtracting, we obtain

$$-\frac{\hbar^2}{2\mathrm{m}}\langle\Delta\psi^0,\tau\rangle+e\langle Q\rho^0,\overline{\psi^0}\tau\rangle=0. \qquad (5.2) \quad \{3GaD2\}$$

Finally,

$$\langle Q\rho^0,\overline{\psi^0}\tau\rangle=\langle\phi^0\psi^0,\tau\rangle, \qquad (5.3) \quad \{3sp\}$$

since $\rho^0=-\Delta\phi^0$. Hence, we can rewrite (5.2) as the variational identity

$$\langle-\frac{\hbar^2}{2\mathrm{m}}\Delta\psi^0+e\phi^0\psi^0,\tau\rangle=0,\qquad \tau\in\mathcal{C}^0. \qquad (5.4) \quad \{3GaD22\}$$

Now we can prove the Schrödinger equation (1.6).

{lse}

Lemma 5.1. *ψ^0 is the eigenfunction of the Schrödinger operator $H=-\frac{\hbar^2}{2\mathrm{m}}\Delta+e\phi^0$:*

$$H\psi^0=\lambda\psi^0, \qquad (5.5) \quad \{3Hpsi\}$$

where $\lambda\in\mathbb{R}$.

Proof. First, $H\psi^0$ is a well-defined distribution, since $\phi^0,\psi^0\in L^2$ by (3.4), and hence $\phi^0\psi^0\in L^1$. Second, $\psi^0\neq 0$, since $\psi^0\in M$ and $Z>0$. Hence, there exists a test function $\theta\in C^\infty(T^3)\setminus\mathcal{C}^0$; i.e.,

$$\langle\psi^0,\theta\rangle\neq 0. \qquad (5.6) \quad \{3test\}$$

As a result, we have

$$\langle(H-\lambda)\psi^0,\theta\rangle=0. \qquad (5.7) \quad \{3test2\}$$

for an appropriate $\lambda\in\mathbb{C}$. However, $(H-\lambda)\psi^0$ also annihilates $\mathcal{C}^0$ by (5.4), and hence it annihilates the whole space $C^\infty(T^3)$. This implies (5.5) in the sense of distributions with a $\lambda\in\mathbb{C}$. Finally, (5.5) gives

$$\langle H\psi^0,\psi^0\rangle=\lambda\langle\psi^0,\psi^0\rangle, \qquad (5.8) \quad \{3Hpsi2\}$$

where the left-hand side is well-defined, because $\psi^0\in H^1$ and $\psi^0\in L^4$, while $\phi^0\in L^2$. Therefore, $\lambda\in\mathbb{R}$, since the potential is real. ■

This lemma implies equation (1.6) with $\hbar\omega^0 = \lambda$. The proof of assertion ii) of Theorem 3.2 is complete.

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