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Intervention in a conference / *Intervention en colloque*

# Some open mathematical problems concerning charged quantum particles

## *Quelques problèmes mathématiques ouverts sur les particules quantiques chargées*

**Mathieu Lewin** [a]

[a] CEREMADE, CNRS and Université Paris Dauphine - PSL, Place de Lattre de Tassigny, 75 016 PARIS, France

*E-mail:* mathieu.lewin@math.cnrs.fr

**Abstract.** I present some open mathematical problems concerning electrons in quantum mechanics and charged particles in general. After discussing the Schrödinger Hamiltonian describing atoms and molecules with classical nuclei, I turn to infinite systems and in particular to the homogeneous electron gas.

**Résumé.** Je présente quelques problèmes mathématiques ouverts concernant les électrons en mécanique quantique et les particules chargées en général. Après avoir discuté de l'hamiltonien de Schrödinger décrivant les atomes et les molécules avec des noyaux classiques, je considère les systèmes infinis et en particulier le gaz homogène d'électrons.

**Keywords.** Schrödinger equation, Coulomb systems, Homogeneous electron gas.

**Mots-clés.** Équation de Schrödinger, Systèmes coulombiens, Gaz d'électrons homogène.

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## 1. Introduction

In my talk at the Institut Henri Poincaré in July 2024 [1], I have discussed some open mathematical problems concerning charged quantum systems. I should first mention that an open mathematical problem need not be considered an open problem from the point of view of physics. Many questions that are extremely difficult to solve rigorously are considered to be fully understood by physicists, whether because of physical intuition, the existence of exact results on simpler models, or with the help of powerful numerical simulations.

So why should we care about proving things with full mathematical rigor? A first obvious reason is that a mathematical proof provides a kind of "seal of quality", that is, a stronger truth about the model under consideration. However, most mathematical physicists feel that adding epsilons and function spaces to an existing convincing physical argument is not the most exciting part of their work. It is much more interesting when the mathematical proof brings a new perspective and thus teaches us new physics. This must be the case in situations where the physical arguments are too vague and do not lead to a clear path for a rigorous proof.

What kinds of physical questions can be answered rigorously? Mathematics is sometimes not very good at dealing with quantitative properties of very particular systems (the chemical properties of a given molecule, for example). It is much better at explaining general (universal)

phenomena for a whole class of models, and at showing connections between situations that look different but are governed by the same mathematical laws.

Let us now turn to the systems of interest for this note, that is, charged particles interacting via the Coulomb interaction

$$\frac{qq'}{|x-x'|}$$

in atomic units. Here $q$, $q' \in \mathbb{Z}$ are the two charges and $x$, $x' \in \mathbb{R}^3$ are the positions of the two particles in consideration. The important mathematical properties of this potential are the singularity at the origin (two particles repel or attract each other strongly when $|x-x'| \ll 1$, depending on the sign of their charges) and the slow decay at infinity (the function $x \mapsto 1/|x|$ is not integrable at infinity in 3D). The singularity at the origin generates an instability for all classical Coulomb systems with opposite charges, leading to a collapse of the system. This is easily resolved by the quantum uncertainty principle. The slow decay of $1/|x|$ at infinity is of a different nature and only causes difficulties for large, macroscopic systems. In fact, every particle in the system feels the Coulomb potential induced by many other particles, even far away, and not just its nearest neighbors. This induces large-scale correlations that could cause the macroscopic object to become unstable. In fact, the existence of matter as we know it has been shown to be a consequence of both screening effects (the charges tend to balance out so that the system is essentially neutral locally, making the potential locally finite) and the fermionic nature of electrons [2]. We will discuss this in more detail below.

The paper is organized as follows. We first discuss open problems concerning the molecular Born–Oppenheimer Schrödinger Hamiltonian describing a finite set of $N$ quantum electrons and $M$ classical nuclei. In Section 3 we turn to infinite systems and, in particular, the homogeneous electron gas.

## 2. Atoms and molecules

Let us start by mentioning some famous open mathematical problems concerning the Schrödinger Hamiltonian of $N$ electrons submitted to an external potential $V : \mathbb{R}^3 \to \mathbb{R}$,

$$H(V,N) = \sum_{j=1}^{N} \frac{-\Delta_{x_j}}{2} + \sum_{j=1}^{N} V(x_j) + \sum_{1 \le j < k \le N} \frac{1}{|x_j - x_k|}, \tag{1}$$

in atomic units. The operator acts on wavefunctions $\Psi(x_1,\sigma_1,\dots,x_N,\sigma_N)$ that are antisymmetric with respect to the exchanges of the position and spin variables $(x_j,\sigma_j) \in \mathbb{R}^3 \times \{\uparrow,\downarrow\}$ of the electrons. We are particularly interested in the case that $V$ describes the potential induced by a finite number $M$ of classical nuclei

$$V(x) = -\sum_{m=1}^{M} \frac{z_m}{|x - R_m|}, \tag{2}$$

where $z_m \in \mathbb{N}$ and $R_m \in \mathbb{R}^3$ are the nuclear charges and positions.

The Hamiltonian (1) has been the subject of much mathematical work, too much to mention with full details. Kato proved in the 50s [3] that for reasonable external potentials $V$, including the one in (2), the above Hamiltonian is well defined on the domain

$$\mathscr{D}(H(V,N)) = \left\{ \Psi : \int |\Psi|^2 + \sum_{j=1}^{N} \int |\Delta_{x_j}\Psi|^2 < \infty \right\}. \tag{3}$$

The integral is here understood in the sense of Lebesgue [4, Chapter 1]. More precisely, this is an integral for the space variables but a sum over the spin variables:

$$\int |\Psi|^2 := \sum_{\sigma_1,\dots\sigma_N \in \{\uparrow,\downarrow\}} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} |\Psi(x_1,\sigma_1,\dots,x_N,\sigma_N)|^2 \,\mathrm{d}x_1 \cdots \mathrm{d}x_N.$$

On the other hand, the Laplacian $\Delta_{x_j}\Psi$ is understood in the sense of distributions [4, Chapter 6]. The operator $H(V,N)$ cannot be defined on a smaller space (in particular it cannot be restricted to smooth functions only), otherwise its spectrum is the whole complex plane [5, Chapter 6]. The domain (3) is is the only one for which $H(V,N)$ is self-adjoint and has a real spectrum. It is nice but somewhat annoying that the abstract theories of Lebesgue integration and weak derivatives are unavoidable in quantum mechanics!

After the pioneering work of Kato, many have worked on establishing spectral properties of $H(V,N)$. Zhislin and his collaborators studied the eigenvalues (bound states energies) and the form of the continuous spectrum in the 60–70s. It was proved in particular that for an atom or a molecule, i.e., $V$ of the form in (2), $H(V,N)$ admits infinitely many bound states below its continuous spectrum whenever $N \leq Z$, where

$$Z := \sum_{m=1}^{M} z_m$$

is the total nuclear charge [6]. In other words, the electrons can be bound to the nuclei as soon as the nuclear charge is greater than or equal to the number of electrons. This is due to the long range of the Coulomb potential, which ensures that any electron escaping to infinity is subject to an attractive force that brings it back to the neighborhood of the nuclei, where the charge is $Z-(N-1)>0$ or more. Later it was proved [7–11] that, on the contrary, there can be only finitely many bound states if $N > Z$, and in fact none at all if $N$ is too large. This confirms the obvious intuition that a finite set of nuclei can bind only a finite number of electrons.

Mathematical physicists then turned to the more precise study of the continuous spectrum and of scattering theory. The latter is not so obvious due to the long range of the Coulomb potential [12,13]. Finally, the quantized photon field was included and its influence on the spectrum studied at length [14,15] (in this case only the ground state remains and the higher excited states become resonances). Below we discuss in Section 3 the limit of a large number of electrons and nuclei, $N, M \to \infty$.

### 2.1. *Ionization conjectures*

If we plot the experimental ground state energy of an arbitrary atom of the periodic table as a function of the number of electrons $N$, we obtain a curve that looks like the ones shown in Figure 1 for the particular cases of oxygen ($Z = 8$) and zinc ($Z = 30$). Let us discuss some general properties of these curves and ask what was rigorously proved for the (non-relativistic) Schrödinger Hamiltonian (1).

#### 2.1.1. *Monotonicity*

A first remark is that the curves are decreasing (more precisely they are non-increasing since they can be constant). This is because adding an electron can only make the ground state energy smaller. In the worse case the additional electron escapes to infinity where it can have an arbitrary small energy. The monotonicity of the curve is not difficult to prove for the Hamiltonian $H(V,N)$. To make things more explicit, let us denote by

$$E(V,N) = \inf_{\Psi} \langle \Psi | H(V,N) | \Psi \rangle = \min \sigma(H(V,N))$$

the ground state energy of the system, which equals the minimum of the spectrum of the operator $H(V,N)$. When the infimum is attained, $E(V,N)$ is an eigenvalue (if $N$ electrons can be bound by $V$). If this is not the case, $E(V,N)$ is part of the continuous spectrum. In fact, the HVZ theorem [6,17,18] states that the continuous spectrum of $H(V,N)$ equals a half interval and starts when one electron is sent to infinity:

$$\sigma_{\text{cont}}(H(V,N)) = [E(V,N-1),\infty). \tag{4}$$

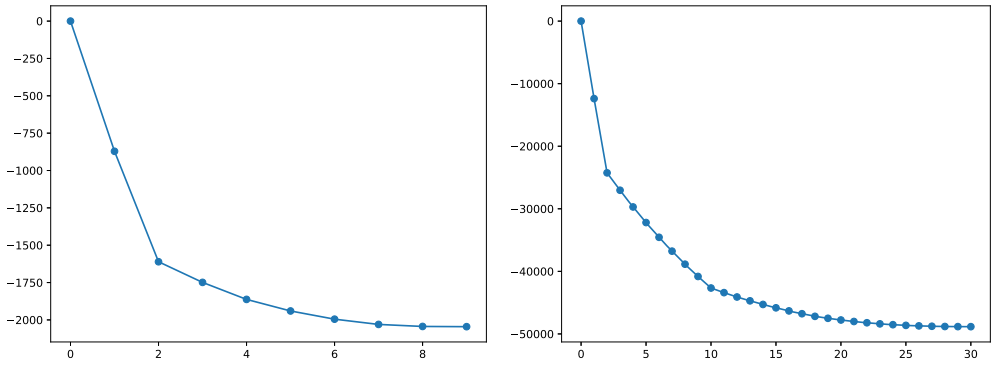


**Figure 1.** Experimental ground state energy (eV) of oxygen (left) and zinc (right) as a function of the number $N$ of bound electrons, according to the NIST database [16]. The curve is constant on the right of the last value of $N$ appearing in the graph, that is, the mentioned atoms do not seem to be able to bind more electrons.

This property is valid for any potential $V$ that tends to 0 at infinity [5, Chapter 6], hence for any Coulomb potential of the form (2). Of course, the latter implies $E(V,N) \leq E(V,N-1)$ for all $N \in \mathbb{N}$ (with the convention $E(V,0) = 0$), which is the observed monotonicity.

2.1.2. *Maximum ionization*

When $N$ exceeds $Z$ by a few units, the ionization curves become flat, meaning that a given nucleus can only accept a few electrons more than its charge. For example, oxygen seems to be able to bind 9 electrons, but not 10. This is of course specific to Coulomb, since a potential $V$ decaying slower than $-1/|x|$ can bind an arbitrarily large number of electrons. That the function $N \mapsto E(V,N)$ becomes constant at some point is quite difficult to prove. This was done in the papers [7–11] mentioned above. But proving that this happens starting from $Z + C$ with a reasonable constant $C$ turned out to be extremely hard and is still open today.

**Open Problem 1 (Maximal ionization).** *Prove that the maximal number of electrons that a molecule can bind satisfies*

$$N_{\max} \leq Z + CM \tag{5}$$

*where $M$ is the number of (classical) nuclei, $Z = \sum_{m=1}^{M} z_m$ is the total nuclear charge, and $C$ is a universal reasonable constant (ideally $C = 1$ or $C = 2$).*

Of course, for heavy nuclei we should take relativistic effects into account, which we completely neglect here. If we let $Z$ and $N$ be arbitrarily large and look at the non-relativistic Hamiltonian $H(V,N)$, then no proof of (5) has been provided yet, even with a crazy constant like $C = 10^{100}$. The conjecture is due to Lieb in the 80s and is discussed in detail in the recent chapter [19]. It is also *Problem 10C* in a famous list by Simon [20] published exactly 40 years ago.

Why should we be interested in this conjecture? The main interest of this problem is that it must follow from a *complicated interplay between the Coulomb forces and the fermionic nature of the electrons*. In fact, as we will see below, the conjecture is known to be wrong if the electrons are replaced by charged bosons! A classical nucleus of charge $Z$ can bind $N_{\max} \approx 1.21\, Z$ bosonic electrons for $Z \gg 1$ [21,22]. Consequently, any proof of the conjecture would require a deep understanding of how the Pauli principle is interrelated with the Coulomb forces. Any progress in this direction would tell us more about the nature of quantum matter.

Let us briefly discuss some important partial results concerning $N_{\max}$. The best bound currently known is due to Lieb in [11] and states that $N_{\max} < 2Z + M$. This nice proof uses

some special properties of the Coulomb potential, but no particle statistics (it works the same for bosons). Better bounds are known for atoms ($M = 1$). Taking into account the Pauli principle, Nam [23] obtained $N_{\max} < 1.22\ Z + 3Z^{1/3}$. If we restrict ourselves to $Z \leq 118$ as in the current periodic table, we get the somewhat unreasonable estimate

$$N_{\max} \leq Z + 40, \quad \text{for } Z \leq 118.$$

Still for $M = 1$ it was proved that $N_{\max} = Z + o(Z)$ in [24,25], which was later improved to $N_{\max} = Z + O(Z^{5/7})$ in [26,27]. Finally, Solovej managed to prove the conjecture in Hartree–Fock theory in a very delicate work [28,29], but with a huge constant $C$. The proof seems very difficult to generalize to the many-body problem.

2.1.3. *Convexity*

Let us return to the experimental ionization energies in Figure 1. Another property that stands out is that the curves are convex. This corresponds to the rather obvious fact that if we start from the right (say at $N = Z$) and remove the electrons one by one, we will first catch the one that is least bound to the nuclei, i.e., for which the ionization energy is the smallest in absolute value. As we remove more electrons, the energy we need pay should increase, because the core electrons are harder to remove than the valence electrons. The monotonicity of the ionization energy $N \mapsto |E(V,N) - E(V,N-1)|$ is exactly the observed convexity.

The obvious caveat to this intuitive argument is that, due to interactions, when we remove an electron, the remaining electrons will change their state to accommodate the missing electron. The new ionization energies, in principle, have nothing to do with those with an extra electron. A little argument shows that the ground state energy is always convex in $N$ for a non-interacting system, so here we try to *understand how correlation affects ionization energies*.

**Open Problem 2 (Convexity).** *Find the class of external potentials $V$'s for which the energy $N \mapsto E(V,N)$ is convex, that is, satisfies*

$$E(V,N) - E(V,N-1) \leq E(V,N+1) - E(V,N), \quad \forall N \in \mathbb{N}. \tag{6}$$

The importance of this problem was first mentioned in the context of Density Functional Theory by Perdew et al. [30] in 1982. In [31, Chapter 4], Parr and Yang stated the conjecture explicitly for all atoms and molecules, that is, for all $V$ of the form (2). Lieb stated it for all possible potential $V$ in [32, *Question 7*]. Simon mentions it only for atoms, as *Problem 10A* in his famous list of open questions [20] already mentioned above.

Despite the convexity of all experimental curves for atoms, we only have counterexamples for simpler systems. Lieb gave a counterexample to the inequality (6) for $N = 2$ when the Coulomb repulsion is replaced by a hard core. Ayers recently generalized this argument to the Riesz interaction $1/|x-y|^s$ with $s > 2\log 2/\log 3 \approx 1.26$ [33]. Other negative results concern particles interacting with a repulsive harmonic interaction in a harmonic trap [34,35], the 1D Hubbard model [36], or a system in nuclear physics [37].

While preparing the talk last July, I realized that a counterexample for the Coulomb interaction can be provided based on results I obtained earlier in a collaboration [38] with Simone Di Marino and Luca Nenna. This is now described in detail in the new article [39]. Our counterexample to the convexity (6) is for $N = 3$ and it has $M = 6$ nuclei placed very far apart but of very small charges $z_m \ll 1$. This shows that the convexity in $N$ cannot be true for arbitrary potentials $V$, as Lieb suggested in [32]. However, the problem remains completely open for physical nuclei of integer charge. This recent work tells us that the situation is even more complicated than expected, and a mathematical explanation of why convexity is universally observed in experiments remains to be found. Note that the particle statistics does not play an important role, here. The counterexample of [39] also works for charged bosons.

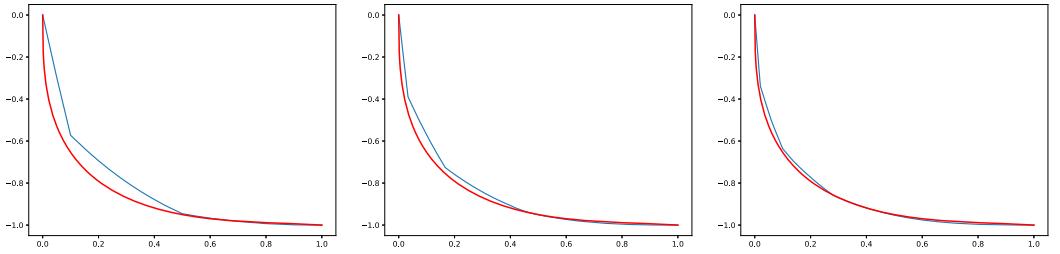

**Figure 2.** Experimental atomic ground state energies for $Z = 20$ (left), $Z = 60$ (center) and $Z = 100$ (right) according to the NIST database [16], plotted together with the Thomas–Fermi energy curve in red, all as functions of $N/Z$ for $N \leq Z$. The energies are renormalized in the manner $E(-Z/|x|, N)/|E(-Z/|x|, Z)|$ and $e_{\mathrm{TF}}(\kappa)/|e_{\mathrm{TF}}(1)|$, that is, divided by the last energy so that the curves all end up at $-1$.

### 2.1.4. *The large-$Z$ limit for fermions and bosons*

Next, we briefly discuss the limit of large nuclear charge $Z$. For simplicity we assume $M = 1$ (atoms) and we place the nucleus at the origin of space. Looking again at the curves in Figure 1, a natural question arises: do these curves converge in the limit $Z \to \infty$ if we properly renormalize them? The answer is yes, and a proof has been given by Lieb and Simon in [40–42]. If we take $Z \to \infty$ and at the same time $N \to \infty$ while fixing $\kappa = N/Z$, we end up with Thomas–Fermi theory. The formal statement is

$$E(-Z/|x|, N) \underset{\substack{N,Z\to\infty \\ \frac{N}{Z}\to\kappa}}{\sim} E_{\mathrm{TF}}(-Z/|x|, N), \tag{7}$$

where

$$\begin{aligned} E_{\mathrm{TF}}(-Z/|x|, N) &= \inf_{\substack{\rho\geq 0 \\ \int_{\mathbb{R}^3}\rho = N}} \left\{ c_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}}\,\mathrm{d}x - Z\int_{\mathbb{R}^3} \frac{\rho(x)}{|x|}\,\mathrm{d}x + \frac{1}{2}\iint_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y \right\} \\ &= Z^{\frac{7}{3}} e_{\mathrm{TF}}\left(\frac{N}{Z}\right), \end{aligned} \tag{8}$$

and $c_{\mathrm{TF}} = (3/10)(6\pi^2)^{2/3}$. Here $\rho$ is the total density of the system and

$$e_{\mathrm{TF}}(\kappa) = \inf_{\substack{\nu\geq 0 \\ \int_{\mathbb{R}^3}\nu = \kappa}} \left\{ c_{\mathrm{TF}} \int_{\mathbb{R}^3} \nu(x)^{\frac{5}{3}}\,\mathrm{d}x - \int_{\mathbb{R}^3} \frac{\nu(x)}{|x|}\,\mathrm{d}x + \frac{1}{2}\iint_{\mathbb{R}^6} \frac{\nu(x)\nu(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y \right\}. \tag{9}$$

To go from the first to the second line in (8), we have introduced the rescaled density $\nu(x) = Z^{-2}\rho(Z^{-1/3}x)$. In this limit the kinetic energy dominates and the system is paramagnetic (spins up and down are occupied with density $\rho/2$). To illustrate the convergence (7) on real data, we have plotted the experimental energy curves for $Z = 20, 60, 100$ together with the Thomas–Fermi curve $\kappa \mapsto e_{\mathrm{TF}}(\kappa)$ in Figure 2.

The Thomas–Fermi energy curve satisfies all the previously observed properties. Namely, it is convex decreasing and constant for $\kappa = N/Z \geq 1$. The convexity comes from the facts that the functional in the curly brackets in (9) is convex in the rescaled density $\nu$ and that $\kappa$ appears as a linear constraint. That it admits no ground state for $N/Z > 1$ is not easy and was proved in [41,42]. Since all the desired properties are known to be valid in the limit $Z \to \infty$, it is natural to try to bring this information back to finite $Z$ and get some results for the Schrödinger Hamiltonian, by a kind of perturbative argument. This turned out to be very difficult and so far was only achieved in Hartree–Fock theory [29].

Many more questions inspired by Thomas–Fermi theory can be posed concerning the Schrödinger Hamiltonian. We refer to [43] for a discussion of the radius of atoms and to [44] concerning the periodicity properties of the periodic table.

As a final comment, we mention that for bosonic electrons, the limit is the Hartree energy [22,45–47], given by

$$\inf_{\int_{\mathbb{R}^3}|\phi|^2=N}\left\{\frac{1}{2}\int_{\mathbb{R}^3}|\nabla\phi(x)|^2\,\mathrm{d}x - Z\int_{\mathbb{R}^3}\frac{|\phi(x)|^2}{|x|}\,\mathrm{d}x + \frac{1}{2}\iint_{\mathbb{R}^6}\frac{|\phi(x)|^2|\phi(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y\right\} = Z^3\,e_{\mathrm{H}}\left(\frac{N}{Z}\right)$$

with $\phi$ the macroscopic condensate wavefunction and

$$e_{\mathrm{H}}(\kappa) = \inf_{\int_{\mathbb{R}^3}|\chi|^2=\kappa}\left\{\frac{1}{2}\int_{\mathbb{R}^3}|\nabla\chi(x)|^2\,\mathrm{d}x - \int_{\mathbb{R}^3}\frac{|\chi(x)|^2}{|x|}\,\mathrm{d}x + \frac{1}{2}\iint_{\mathbb{R}^6}\frac{|\chi(x)|^2|\chi(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y\right\}. \tag{10}$$

This time we used $\phi(x) = Z^2\chi(Zx)$. The previous minimization admits ground states for $\kappa \le \kappa_c$ and none for $\kappa > \kappa_c$, where $\kappa_c \approx 1.21$. A perturbative argument proved that $N_{\max}/Z \to \kappa_c$ in the limit $Z \to \infty$, so bosonic atoms can bind many more electrons than real atoms [21,22]. Note that the limiting energy curve is still convex, suggesting that the convexity is not so closely related to the particle statistics.

## 2.2. *Chemical reactions*

Now let us look at another question that is closer to quantum chemistry. Lieb and Thirring proved in [48] that *all neutral molecules can bind*, at zero temperature. To state the result correctly, we include the nuclear energy and define the total energy of a molecule by

$$E_{\mathrm{mol}}(z_m, R_m, N) := E(V, N) + \sum_{1\le k<m\le M}\frac{z_k z_m}{|R_k - R_m|} \tag{11}$$

where, of course, $V$ is given by (2). The statement is that when $N = Z = \sum_{m=1}^M z_m$, the function $(R_1,\dots,R_M) \mapsto E_{\mathrm{mol}}(z_m, R_m, N)$ reaches its minimum. More precisely, the lowest energy of a molecule is always strictly lower than when it is broken into pieces:

$$\min_{R_1,\dots,R_M\in\mathbb{R}^3} E_{\mathrm{mol}}(z_m, R_m, N) < \liminf_{\max_{1\le k<m\le M}|R_k-R_m|\to\infty} E_{\mathrm{mol}}(z_m, R_m, N). \tag{12}$$

The result is very intuitive when the molecule breaks into two charged pieces, because those have different signs and therefore must attract each other at infinity. The result of [48] concerns the situation where the molecule breaks into neutral clusters. It is proved that those attract with a van der Waals force, which results from an *interplay between correlation and the long range of the Coulomb potential*.

In [49–51] we studied the situation of a molecule that admits two local minima with respect to the nuclear positions $R_1,\dots,R_M$ and asked whether there exists a transition state between them (also called a *mountain pass* and corresponding to a saddle point of the energy functional). This was proved in many situations of physical interest by studying the critical points of the multipole interactions, but not yet in the general case.

**Open Problem 3 (Chemical reactions).** *Prove that for a molecule possessing two local stable configurations (that is, local minima of* $(R_1,\dots,R_M) \in (\mathbb{R}^3)^M \mapsto E_{\mathrm{mol}}(z_m, R_m, N)$*), the isomerization between them happens without breaking the molecule into pieces.*

## 3. Infinite systems, the homogeneous electron gas

Finally, we discuss some open problems for macroscopic Coulomb systems. Although these have been the subject of many studies in the last decades, several fundamental questions are still completely open on the mathematical side.

We should mention the beautiful theory of "stability of matter" by Dyson and Lieb [2,52–55], which led to both deep mathematical results and new physical insights. This concerns the situation where the number of electron diverges, $N \to \infty$, as well as the number of nuclei, $M \to \infty$ but the charges $z_m$ remain bounded. One can choose the positions and charges of the nuclei, for instance place them on a lattice to describe a given material [56,57]. It is also possible to randomly perturb a given lattice (Anderson model) [58]. Finally, one can as well optimize over the number and positions of the nuclei [59] (assuming for instance that they all have the same charge $z_m = z$). In short, it was understood that such systems are always stable, which means that the ground state energy behaves linearly with particle number or volume. This is what is needed to ensure that a macroscopic system does not collapse. Note that for bosonic electrons, the energy behaves like $N^{5/3}$ [60] if the nuclei can be arbitrarily close to each other but it stays of order $N$ if the nuclei have a finite distance to each other [57]. The Pauli principle therefore plays again a crucial role here.

Because of its importance in applications (in particular in Density Functional Theory [31]), the *Homogeneous Electron Gas* (HEG) has also been extensively studied. In this system, the classical nuclei are replaced by a uniform background of fixed positive charge (taken first in a finite domain and then extended to the whole space). Although screening effects still play an essential role, it is less important that the electrons are fermions. The HEG is also stable for charged bosons and even for classical electrons [61,62].

Stability is only the first step in the study of large quantum systems. The next step is to understand the properties of equilibrium states and, in particular, the sudden changes that can happen when varying the temperature or the density. Of particular interest is the lack of uniqueness due to the breaking of translational symmetry, that is expected to arise in the solid phase. Not much is known rigorously about the existence of such phase transitions.

**Open Problem 4 (Phase transitions).** *Prove that translational symmetry is broken for the Homogeneous Electron Gas or with classical point nuclei, at low density and/or low temperature.*

In the case of classical nuclei we can assume, for example, that we have only one kind of nuclei (all of the same charge $z$) and, at $T = 0$, that we are optimizing over the nuclear positions. Remember that they can all bind, as we saw in Section 2.2. It is also possible to take a finite number of charges $z_1, \dots, z_M$. We can then fix the average density of each species or just optimize over the charges as well.

Showing that translational symmetry is broken seems very hard. This requires first defining what it means to be an *infinite equilibrium state*, since the Gibbs state is always unique at $T > 0$ and non-uniqueness can only occur for an infinite system. Defining such infinite states is a hard problem because the equilibrium equations usually include the interaction potential between each electron and the rest of the system, which is typically a divergent integral or series due to the long range of the Coulomb interaction. Delicate compensations are expected due to screening effects, but proving that they actually occur is very difficult. For the 3D Coulomb potential, infinite equilibrium states have so far only been constructed for classical electrons at $T = 0$ in [62, Theorem 28] and for $T \gg 1$ in [63].

Even for short-range interactions we know very little concerning the existence of phase transitions. All existing rigorous results in this direction (e.g., [64,65]) are for very special systems and rely on specific methods that cannot be easily adapted to Coulomb systems. So the situation

is rather embarrassing! We have no mathematical intuition as to why translation invariance should be broken, nor even a strategy as to how to prove it. This is one of the most important open problems in mathematical physics.

Showing the breaking of translations is of course only a first step. We expect that the system will be a proper solid, that is, periodic with a non-trivial period. This is often referred to as *Wigner's crystallization conjecture* [66,67].

**Open Problem 5 (Wigner crystallization).** *Prove that at low temperature and/or low density, infinite equilibrium states are periodic. For the HEG, it must be the Body-Centered-Cubic lattice.*

For classical electrons, the conjectured periodic arrangement should arise from the fact that they repel each other and thus seek to minimize the repulsion energy by maximizing their relative distances, while at the same time being attracted to the uniform positive background. In the quantum case, this picture should remain true at low density, since the kinetic energy $1/a^2$ of an electron localized in a periodic cell of side length $a$ remains small compared to the repulsion energy $1/a$ between neighboring electrons. Unfortunately, this intuitive image has never been rigorously justified for either classical or quantum electrons. The only system that is well understood is the one-dimensional HEG (with the interaction $-|x-y|$), for which crystallization was proved at all densities and temperatures [68–72].

For classical electrons, the crystallization conjecture has interesting links with number theory. This is because if we take an infinite lattice $\mathscr{L}$ of particles interacting with the Riesz potential $1/|x-y|^s$ with $s > d$ (the space dimension), the interaction energy of each particle with the rest of the system equals

$$\zeta_{\mathscr{L}}(s) = \frac{1}{2} \sum_{z \in \mathscr{L} \setminus \{0\}} \frac{1}{|z|^s}.$$

This is called the *Epstein Zeta function* and it is a generalization of the Riemann Zeta to higher dimensions. The series converges only for $s > d$ but the function admits a meromorphic continuation to the whole complex plane with a unique pole at $s = d$. This continuation is still denoted by $\zeta_{\mathscr{L}}(s)$. For $s < d$ it is known that $\zeta_{\mathscr{L}}(s)$ is nothing but the energy obtained by inserting a uniform background to compensate the divergence of the series [62, Section IV]. The analytic continuation allows us to place the long and short range cases into the same theory.

In this direction, we would like to mention the recent result [73] that gave the 2022 Fields medal to Maryna Viazovska, where Wigner crystallization was proved in dimensions $d = 8$ and $d = 24$, for all $s \geq d - 2$ [74], hence including the "Coulomb" potential of those dimensions. Dimensions 8 and 24 are special because there exists a specific lattice $\mathscr{L}$, called "universally optimal", that works for all $s$. The same phenomenon is expected in 2D with the triangular lattice, but not proved yet. In 3D there exists no universally optimal lattice and one expects either BCC or FCC depending on the value of $s$ [67]. Apart from 1D, nothing is known in the quantum case.

It seems reasonable to expect that freezing is a universal phenomenon, in dimension 3, but it can still occur in many different ways. The phase diagram of the HEG is still being carefully studied numerically. For a long time it was thought that the system could be a ferromagnetic Wigner crystal, a ferromagnetic liquid, and a paramagnetic liquid. However, recent simulations indicate that the ferromagnetic fluid phase may not exist [75,76]. More transitions could also occur in the solid phase (e.g., an antiferromagnetic crystal). In the case of Hartree–Fock, thorough numerical studies [77–79] predicted many transitions in the solid region, including exotic "incommensurate" phases.

**Open Problem 6 (Phase diagram).** *Develop mathematical tools to study the phase diagram of the HEG and other materials.*

## 4. Conclusion

We have discussed some open mathematical problems concerning charged quantum particles. For atoms and molecules, we focused on the ionization curves obtained when electrons are added or removed from the system in its ground state. Many other open problems could have been mentioned, in particular concerning the inclusion of relativistic effects or the description of time-dependent phenomena. In another direction, we insisted on the poor rigorous understanding we have of macroscopic Coulomb systems. Phase transitions such as freezing occur experimentally for many Coulomb systems, but there is currently no mathematical tool to rigorously prove this happens. A simple question is why table salt has the structure we know and this must follow from Schrödinger's equation.

## Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

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