20

Many charges, stability of matter

In the low-energy sector, to an excellent approximation, the world consists of photons, electrons, and nuclei. To simplify the forthcoming discussion, let us consider only one species of nuclei with charge eZ, $Z = 1, 2, \dots$. In fact, we also assume that the nuclei are infinitely heavy and located at positions $r_1, \dots, r_K \in \mathbb{R}^3$. This is hardly realistic, but not of central importance for the stability issues studied here. We also ignore nuclear spins. To include them would require yet another layer of considerations. With these assumptions we have an arbitrary number of photons, N electrons, and K nuclei governed by the Hamiltonian

$$H = \sum_{j=1}^{N} \frac{1}{2m} \big(\sigma_j \cdot (p_j - eA_\varphi(x_j)\big)^2 + H_{\mathrm{f}} + V_{\varphi\mathrm{coul}}\,, \tag{20.1}$$

compare with (13.39). σ_j are the Pauli spin matrices for the j-th electron. Since electrons are fermions, the corresponding Hilbert space is

$$\mathcal{H} = P_{\mathrm{a}}\big(L^2(\mathbb{R}^3, \mathbb{C}^2)^{\otimes N}\big) \otimes \mathcal{F} \tag{20.2}$$

with P_{a} denoting the projection onto the subspace of antisymmetric wave functions. $V_{\varphi\mathrm{coul}}$ is the smeared Coulomb potential, cf. (13.17), which in the case considered here is given through

$$V_{\varphi\mathrm{coul}}(x_1, \dots, x_N) = e^2 \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 |k|^{-2} \Big(\sum_{1 \le i < j \le N} \mathrm{e}^{\mathrm{i}k\cdot(x_i - x_j)} - Z \sum_{i=1}^{N} \sum_{j=1}^{K} \mathrm{e}^{\mathrm{i}k\cdot(x_i - r_j)} + Z^2 \sum_{1 \le i < j \le K} \mathrm{e}^{\mathrm{i}k\cdot(r_i - r_j)} \Big)\,. \tag{20.3}$$

One of the most basic facts about nature, which the Hamiltonian (20.1) should better explain, is the apparent stability of ordinary matter over extremely long periods of time. It has become customary to divide the issue roughly into

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(i) atomic stability,
(ii) energy stability (or H-stability),
(iii) thermodynamic stability.

An atom is the special case of (20.1) with $K = 1$ (hence $r_1 = 0$) and N, Z arbitrary. *Atomic stability* means that the ground state for H looks like what we know from real atoms in nature. In particular, provided that $N < Z + 1$, or perhaps $N \leq Z + 1$ admitting a negatively charged ion, H has a ground state eigenvector with an exponentially localized electronic density. Also the ultraviolet cutoff should not have to be fine-tuned. Our understanding of the stability of atoms and molecules within nonrelativistic QED has advanced spectacularly over the past few years. An overview is provided in section 20.1.

Energy stability and *thermodynamic stability* refer to the property that matter at the human scale is (volume) extensive: Adding two buckets of water of 10 liters each merely results in 20 liters of water. Since now many molecules are involved, (20.1) is to be considered for large N with $N \cong KZ$, $Z \leq 100$. For an energy stable system, the volume of the combined system in its ground state is at least as large as the sum of the volumes of the subsystems. It is more convenient to re-express this property in energetic terms. If $E(N; K, r_1, \ldots, r_K)$ denotes the ground state energy of H in (20.1), then for an H-stable system

$$E(N; K, r_1, \ldots, r_K) \geq -c_0 \, (N + K) \tag{20.4}$$

with suitable $c_0 \geq 0$ independent of the location of the nuclei. In fact, such a bound obviously holds, since

$$H \geq V_{\varphi\text{coul}} \geq -\frac{1}{2}\Big(\int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 |k|^{-2} \Big)(e^2 N + e^2 Z^2 K) \, . \tag{20.5}$$

While correct, (20.5) teaches us little about the physics involved, since the bound is cutoff-dependent and is not of the order of one Rydberg, as expected.

The condition (20.4) overlooks the fact that even when the electrons are stripped off to infinity they still carry a self-energy. Denoting as before the self-energy of a single electron by E_{self}, the sharper stability condition is

$$E(N; K, r_1, \ldots, r_K) - N E_{\text{self}} \; \geq \; -c_1 \, (N + K) \tag{20.6}$$

with some suitable constant c_1 independent of the location of the nuclei. Hopefully c_1 is of order of a Rydberg and less sensitive to the cutoff than c_0. Energy stability, as far as aspects of the quantized radiation field are involved, is discussed in section 20.3.

As the name indicates, thermodynamic stability means that the thermodynamic potentials are volume extensive. In particular, the thermodynamic pressure, i.e. the force per unit area on the confining container, is in essence size independent.

For proper statistical mechanics also the nuclei should have a finite mass. In our context a natural model would be to assume charge neutrality, i.e. $N = KZ$, and that the nuclei form a regular crystal lattice. Then one aspect of thermodynamic stability is a ground state energy proportional to the number of particles, which requires (20.6) to be augmented by an upper bound linear in $N + K$. We refer to the notes at the end of the chapter for further details.

No surprise, energy and thermodynamic stability are best understood in the case when the interaction with the radiation field is neglected. This raises the question: In what sense is the standard N-body Coulomb Hamiltonian a good approximation to (20.1)? In the classical context we discussed this problem rather exhaustively in section 11.2. Quantum mechanics adds a layer of difficulty, as will be explained in section 20.2.

20.1 Stability of atoms and molecules

The number of electrons, N, is regarded as fixed and the goal is to understand under what conditions, in their lowest-energy state, they are all bound to the nuclei. For this purpose the interaction between nuclei can be dropped. We also ignore the smearing of the Coulomb potential. On the other hand, we want to allow a variation in the nucleon charge, i.e. the j-th nucleus is located at r_j and has charge eZ_j, $Z_j > 0$, $j = 1, \dots, K$. With these modifications, the Hamiltonian reads

$$H^{\mathrm{V}}(N) = \sum_{j=1}^{N} \frac{1}{2m} \big(\sigma_j \cdot (p_j - eA_\varphi(x_j))\big)^2 + H_{\mathrm{f}} + \sum_{1 \le i < j \le N} e^2 (4\pi |x_i - x_j|)^{-1} - \sum_{i=1}^{N} \sum_{j=1}^{K} e^2 Z_j (4\pi |x_i - r_j|)^{-1} \,. \tag{20.7}$$

The form factor ensures a smooth cutoff at large k, but $\widehat{\varphi}(0) = (2\pi)^{-3/2}$ as it should. The bottom of the spectrum for $H^{\mathrm{V}}(N)$ is

$$E^{\mathrm{V}}(N) = \inf \sigma(H^{\mathrm{V}}(N)) = \inf_{\psi, \|\psi\|_{\mathcal{H}}=1} \langle \psi, H^{\mathrm{V}}(N) \psi \rangle_{\mathcal{H}} \,. \tag{20.8}$$

We will have to compare with free electrons whose Hamiltonian is

$$H^0(N) = \sum_{j=1}^{N} \frac{1}{2m} \big(\sigma_j \cdot (p_j - eA_\varphi(x_j))\big)^2 + H_{\mathrm{f}} + \sum_{1 \le i < j \le N} e^2 (4\pi |x_i - x_j|)^{-1} \,. \tag{20.9}$$

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Its lowest energy is denoted by $E^0(N)$. It is unlikely that the effective interaction induced by the photon cloud overrules the combined Coulomb repulsion and Fermi exclusion. Thus $E^0(N) = NE^0(1)$ is expected, but will not be assumed here.

The general strategy is to introduce a suitable notion of the ionization energy $E_{\rm ion}(N)$. Then the binding energy is defined by

$$E_{\rm bin}(N) = E_{\rm ion}(N) - E^{\rm V}(N)\,. \tag{20.10}$$

If $E_{\rm bin}(N) > 0$, the energy interval $\Delta = [E^{\rm V}(N), E_{\rm ion}(N))$ is nonempty and states with an energy distribution supported by Δ should be well localized near the nuclei. Amongst them there will be the stable ground state.

It seems clear how to proceed. If one electron is moved to infinity it has energy $E^0(1)$ and the corresponding lowest-energy state of $H^{\rm V}(N)$ has the energy $E^{\rm V}(N-1) + E^0(1)$. Of course it could be energetically more favorable to move two electrons to infinity, etc. Thus

$$E_{\rm ion}(N) = \min_{1\le N'\le N} \left\{E^{\rm V}(N-N') + E^0(N')\right\} \tag{20.11}$$

with the convention $E^{\rm V}(0) = 0$. Note that if the interaction with the photon field is turned off, formally setting $\widehat{\varphi} = 0$, then $E^0(N) = 0$ and (20.11) agrees with the standard definition of the ionization energy for the Coulomb Hamiltonian.

There is a more direct way of moving electrons to infinity. As in chapter 16, we regard $\psi(x)$ as a $\mathbb{C}^{2N} \otimes \mathcal{F}$-valued wave function, $x = (x_1, \ldots, x_N)$. We define P_R as the projection on the subspace of wave functions satisfying $\psi(x) = 0$ for $|x| < R$. Then the alternative definition is

$$E_{\rm ion}(N) = \lim_{R\to\infty} \inf \sigma(P_R H^{\rm V}(N) P_R)\,. \tag{20.12}$$

As proved by Griesemer (2002) the definitions (20.11) and (20.12) of the ionization energy agree in the context of the Pauli–Fierz Hamiltonian. Note that with (20.12) it is obvious that $E_{\rm bin} \ge 0$. Also, if $H^{\rm V}(N)$ admits surplus electrons, necessarily $E_{\rm bin} = 0$.

Let us denote by $E_\lambda = E_\lambda(H^{\rm V}(N))$ the spectral resolution of $H^{\rm V}(N)$, i.e. E_λ is the projection corresponding to the energy interval $(-\infty, \lambda]$.

Theorem 20.1 (Exponential localization). *Let $E_{\rm bin}(N) > 0$ and let us choose λ, β such that $\lambda + (\beta^2/2m) < E_{\rm ion}(N)$, $E^{\rm V}(N) \le \lambda$, $\beta > 0$. If $E_\lambda \psi = \psi$, then*

$$\|{\rm e}^{\beta|x|}\psi\|_{\mathcal{H}} \le c_0 \|\psi\|_{\mathcal{H}}\,. \tag{20.13}$$

The proof is due to Griesemer (2004). In fact, the proof exploits only properties of the Laplacian. As in chapter 16, we regard $\mathcal{H} = L^2(\mathbb{R}^n, \mathcal{H}_{\rm f}) = L^2(\mathbb{R}^n, {\rm d}^n x) \otimes \mathcal{H}_{\rm f}$ with some Hilbert space $\mathcal{H}_{\rm f}$ of "internal degrees of freedom". The operator

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H with domain $D(H)$ is self-adjoint on $\mathcal{H}$. Let $f \in C^\infty(\mathbb{R}^n, \mathbb{R})$ with f and ∇f bounded. The crucial assumption concerns the double commutator

$$[[H, f], f] = -2|\nabla f|^2 \tag{20.14}$$

with f regarded as a multiplication operator. Note that (20.14) holds in the case $\mathcal{F} = \mathbb{C}$ and $H = -\Delta$. But (20.14) holds also for $H = H^{\mathrm{V}}(N)$ setting $n = 3N$. As before the ionization threshold for H is

$$E_{\mathrm{ion}} = \lim_{R\to\infty} \inf \sigma(P_R H P_R)\,. \tag{20.15}$$

Proposition 20.2 *Let H satisfy (20.14) and let $\lambda + \beta^2 < E_{\mathrm{ion}}$, $\beta > 0$. Then*

$$\|\mathrm{e}^{\beta|x|} E_\lambda(H)\|_{\mathcal{H}} < \infty\,. \tag{20.16}$$

Let us return to the existence of a ground state for $H^{\mathrm{V}}(N)$. If $E_{\mathrm{bin}} > 0$, the exponential localization is a favorable indication. But it could happen that more and more photons are bound by the electrons. Thus we need a soft photon bound of the type of Theorem 15.1. The proof is now considerably more demanding and established by Griesemer, Lieb and Loss (2001).

Theorem 20.3 (Existence of a ground state). *If $E_{\mathrm{bin}}(N) > 0$, then $H^{\mathrm{V}}(N)$ has a ground state.*

Because of Pauli exclusion and spin, no obvious positivity is available which would ensure uniqueness. Note that there is no restriction on the coupling strength e. Also, by Proposition 20.2, the ground state is exponentially localized with length less than $1/\sqrt{2mE_{\mathrm{bin}}(N)}$.

The existence of a ground state is reduced to the issue of whether $E_{\mathrm{bin}}(N) > 0$. While the statement looks innocent and seems to require only the clever choice of a wave function, the actual construction is ingenious and has been achieved only very recently by Lieb and Loss (2003). The main obstacle is the, in position space, nonlocal nature of the photon kinetic energy.

Theorem 20.4 (Strictly positive binding energy). *Let eZ_{tot} be the total nuclear charge, $Z_{\mathrm{tot}} = \sum_{j=1}^K Z_j$. If*

$$N < Z_{\mathrm{tot}} + 1\,, \tag{20.17}$$

then $E_{\mathrm{bin}}(N) > 0$.

In nature ions carrying one, or perhaps two, extra electrons are rather common. Such fine chemical features are difficult to access. In fact, even on the level of the Coulomb Hamiltonian the excess charge for stable ions is poorly understood.

20.2 Quasi-static limit

We plan to investigate under what limiting conditions the many-particle Pauli–Fierz Hamiltonian can be approximated by the Coulomb Hamiltonian with possible corrections. The implementation of the limit (11.8) on the quantum level has not yet been attempted. Thus we have to be satisfied with the more down-to-earth limit $c \to \infty$ already discussed briefly at the beginning of section 11.2. $c \to \infty$ means that the interaction between the charges becomes instantaneous, a principle on which the Coulomb Hamiltonian is built. To study this limit we had better reintroduce the velocity of light, which amounts to

$$H(c) = \sum_{j=1}^{N} \frac{1}{2m_j} \Big(\sigma_j \cdot \Big(p_j - \frac{1}{\sqrt{c}} e_j A_\varphi(x_j) \Big) \Big)^2 \; + \; V_{\varphi\mathrm{coul}} \; + \; cH_\mathrm{f} \,. \tag{20.18}$$

$A_\varphi(x)$, $V_{\varphi\mathrm{coul}}$, and H_f do not depend on c. The prefactors as written result from reintroducing $\omega(k) = c|k|$. The masses and charges are arbitrary.

c has a dimension. So what we really mean is $|v|/c \to 0$, where v is some characteristic velocity of the charges. Thus either $c \to \infty$ at fixed $|v|$ or $|v| \to 0$ at fixed c. The latter can also be achieved by assuming the particles to be heavy and, hence, by replacing in (20.18) m_j by $\varepsilon^{-2} m_j$, $\varepsilon \ll 1$. On the classical level the limits $c \to \infty$ and $\varepsilon \to 0$ are related through the time scale change t to εt, and thus are completely equivalent. Quantum mechanically the two Hamiltonians are not unitarily related, which reflects the additional scale coming from $\hbar$.

Let us first study the limit $c \to \infty$. Except for normal order the Hamiltonian (20.18) reads

$$\begin{aligned} H(c) = & \sum_{j=1}^{N} \frac{1}{2m_j} p_j^2 \; + \; V_{\varphi\mathrm{coul}} - \frac{1}{\sqrt{c}} \sum_{j=1}^{N} \frac{e_j}{m_j} p_j \cdot A_\varphi(x_j) \\ & - \frac{1}{\sqrt{c}} \sum_{j=1}^{N} \frac{e_j}{2m_j} \sigma_j \cdot B_\varphi(x_j) \; + \; \frac{1}{c} \sum_{j=1}^{N} \frac{e_j^2}{2m_j} \, {:}A_\varphi(x_j)^2{:} + cH_\mathrm{f} \,. \end{aligned} \tag{20.19}$$

$H(c)$ should be compared with the weak coupling Hamiltonian (17.4), written for the long-time scale $\lambda^{-2}\tau$ and with the abbreviation $H_\mathrm{int} = \tilde{Q} \cdot A_\varphi(0)$,

$$H_\lambda = \lambda^{-2} H_\mathrm{at} \; + \; \lambda^{-1} H_\mathrm{int} \; + \; \lambda^{-2} H_\mathrm{f} \,. \tag{20.20}$$

The interaction part H_int satisfies $\langle \Omega, H_\mathrm{int} \Omega \rangle_\mathcal{F} = 0$, which holds also for (20.19), since $\langle \Omega, A_\varphi(x_j)\, \Omega \rangle_\mathcal{F} = 0$, $\langle \Omega, B_\varphi(x_j)\, \Omega \rangle_\mathcal{F} = 0$, and $\langle \Omega, {:}A_\varphi(x_j)^2{:}\, \Omega \rangle_\mathcal{F} = 0$. The central insight of the weak coupling theory is that the correction to H_at results from balancing $\lambda^{-2}(H_\mathrm{int})^2$ with the time averaging due to $\lambda^{-2} H_\mathrm{f}$; compare with

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(17.22). Clearly this balance can be achieved also in (20.19) by considering the long-time scale

$$t = c^2\tau \quad \text{with} \quad \tau = \mathcal{O}(1)\,. \tag{20.21}$$

Then $H_{\rm f}$ has the prefactor c^3, $H_{\rm int}$ the prefactor $c^{3/2}$ with a subleading correction of order c, and $H_{\rm at}$ has the prefactor c^2. The analog of (17.24) becomes

$$K\rho = -\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}L_{\rm at}c^{-1}t}\,\mathrm{tr}_{\mathcal{F}} L_{\rm int}\mathrm{e}^{-\mathrm{i}(c^{-1}L_{\rm at}+L_{\rm f})t} L_{\rm int} P_\Omega]\rho\,. \tag{20.22}$$

In the limit $c \to \infty$ the dependence on $L_{\rm at}$ drops out. In particular, this implies that the correction term must be nondissipative; compare with (17.35) which is evaluated at $\omega = 0$.

Let us first write out the limiting objects. The analog of $H_{\rm at}$ is

$$H_{\varphi\rm coul} = \sum_{j=1}^N \frac{1}{2m_j} p_j^2 + V_{\varphi\rm coul}\,. \tag{20.23}$$

It is corrected by

$$(-i)V_{\varphi\rm darw} = \mathrm{i}\int_0^\infty \mathrm{d}t\ \langle\Omega,\, H_{\rm int}\mathrm{e}^{-\mathrm{i}tH_{\rm f}} H_{\rm int}\Omega\rangle_{\mathcal{F}}\,, \tag{20.24}$$

which upon working out the integrals becomes

$$\begin{aligned} V_{\varphi\rm darw} = &-\sum_{i,j=1}^N \frac{e_i e_j}{m_i m_j}\int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \frac{1}{2k^2}\mathrm{e}^{\mathrm{i}k\cdot x_i}(p_i\cdot Q^\perp(k)\,p_j)\mathrm{e}^{-\mathrm{i}k\cdot x_j} \\ &-\sum_{i,j=1}^N \frac{e_i e_j}{12 m_i m_j}\,\sigma_i\cdot\sigma_j \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \mathrm{e}^{\mathrm{i}k\cdot(x_i - x_j)}, \end{aligned} \tag{20.25}$$

which is the Darwin correction. We set

$$H_{\varphi\rm darw} = H_{\varphi\rm coul} + c^{-2}V_{\varphi\rm darw}\,. \tag{20.26}$$

Note that the integrability condition (17.27) is satisfied, since the integrand in (20.24) is bounded by $(1+t^2)^{-1}$. In contrast to section 17.2, $H_{\rm int}$ has an unbounded factor acting on $\mathcal{H}_{\rm p}$, which necessitates a restriction on the initial wave function. We summarize as

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Theorem 20.5 (Coulomb Hamiltonian and correction). *Let* $\psi \in L^2$ *with* $\langle \psi, H_{\mathrm{coul}}\psi\rangle_{L^2} < \infty$. *Then*

$$\lim_{c\to\infty} \|\big(\mathrm{e}^{-\mathrm{i}H(c)c^2t} - \mathrm{e}^{-\mathrm{i}(H_{\varphi\mathrm{darw}}+cH_{\mathrm{f}})c^2t}\big)\psi\otimes\Omega\| = 0\,. \tag{20.27}$$

Since the limit (20.27) is on the long-time scale c^2, the Darwin correction is meaningfully singled out.

Except for operator ordering, (20.27) is in accordance with the results in section 11.2. However in L_{darw} of (11.27) the kinetic energy is modified and the Coulomb potential is not smeared out, which reflects the fact that limits here and in section 11.2 differ somewhat.

For the limit $m_j \to \infty$ we can also rely on methods developed before. We start with the classical symbol

$$\begin{aligned} H(q,p) = \sum_{j=1}^{N} \Big(&\frac{1}{2m_j}p_j^2 - \varepsilon\frac{e_j}{m_j}p_j\cdot A_\varphi(q_j) \\ &- \varepsilon^2\frac{e_j}{2m_j}\sigma_j\cdot B_\varphi(q_j) + \varepsilon^2\frac{e_j^2}{2m_j}:A_\varphi(q_j)^2:\Big) + V_{\varphi\mathrm{coul}}(q) + H_{\mathrm{f}}\,, \end{aligned} \tag{20.28}$$

$q = (q_1,\dots,q_N)$, $p = (p_1,\dots,p_N)$. The Weyl quantization of $H(q,p)$ is $H(c)$ of (20.18) with m_j replaced by $\varepsilon^{-2}m_j$, where for convenience we returned to $c = 1$. The leading symbol for $H(q,p)$ is

$$H_0(p,q) = \sum_{j=1}^{N}\frac{1}{2m_j}p_j^2 + V_{\varphi\mathrm{coul}}(q) + H_{\mathrm{f}}\,. \tag{20.29}$$

Its ground state band has the projection $P_0(q,p) = 1\otimes P_\Omega$, independent of q,p, and the eigenvalue $e_0(q,p) = \sum_{j=1}^{N}(p_j^2/2m_j) + V_{\varphi\mathrm{coul}}(q)$. Thus, following section 16.4, the Coulomb Hamiltonian can be understood as Peierls' substitution for (20.28). It approximates on the time scale $\varepsilon^{-1}t$ the true unitary evolution projected to $1\otimes P_\Omega$.

To obtain corrections we have to first compute h_1. Since $\langle\Omega, H_{\mathrm{int}}\Omega\rangle = 0$ and since P_0 does not depend on p,q, $h_1 = 0$, in accordance with the previous findings that the Darwin correction is of order ε^{-2}. Thus we need h_2. In section 16.4 no explicit formula was given, since it is already somewhat lengthy. In our particular

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case, many simplifications occur and as a net result one finds that

$$h_2(q,p) = -\sum_{i,j=1}^{N} \frac{e_i e_j}{m_i m_j}\Big(\int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \frac{1}{2\omega^2} (p_i \cdot Q^{\perp}(k) p_j) \mathrm{e}^{\mathrm{i}k\cdot(q_i - q_j)} + \frac{1}{12}(\sigma_i \cdot \sigma_j) \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \frac{k^2}{\omega^2} \mathrm{e}^{\mathrm{i}k\cdot(q_i-q_j)} \Big) . \tag{20.30}$$

While, since in agreement with the previous result, (20.30) is very satisfactory on a formal level, a complete proof has to deal with the fact that the ground state band is not separated by a gap from the remainder of the spectrum. If one is willing to impose a gap by hand through a massive dispersion ω, then a suitable version of the results described in section 16.4 becomes available. The picture so derived is somewhat different from the $c \to \infty$ limit: the almost invariant subspace is tilted by order ε relative to $(1 \otimes P_\Omega)\mathcal{H}$. Over the time scale $\varepsilon^{-2}t$ the motion in this subspace is governed by $h_0 + \varepsilon^2 h_2$.

20.3 H-stability

For the (no-cutoff) Coulomb Hamiltonian

$$H_{\mathrm{coul}} = \sum_{j=1}^{N} \frac{1}{2} p_j^2 + V_{\mathrm{coul}} ,$$

$$V_{\mathrm{coul}} = \frac{e^2}{4\pi}\Big(\sum_{1\le i<j\le N} |x_i - x_j|^{-1} - Z \sum_{i=1}^{N}\sum_{j=1}^{K} |x_i - r_j|^{-1} + Z^2 \sum_{1\le i<j\le K} |r_i - r_j|^{-1} \Big) , \tag{20.31}$$

the H-stability is a famous result by Dyson and Lenard. An independent proof was achieved by Lieb and Thirring, who succeeded in a fairly realistic estimate of the stability constant. For stability to hold the electrons must satisfy the Pauli exclusion principle, as they do in nature. For bosons the energy would decrease as $-N^{5/3}$. If the nuclei have a finite mass, for a H-stable system at least one of the two species must be fermions.

To extend H-stability to the realm of nonrelativistic quantum electrodynamics, one has to establish a lower bound on $H^{\mathrm{V}}(N) = H$, see (20.7), linear in $K + N$. Note that for spinless electrons $H \ge H_{\mathrm{coul}}$ by the diamagnetic inequality (14.69) and one is back to the H-stability in (20.31). Thus the difficult point is to deal with electron spin and the associated magnetic energy. The Schrödinger representation, as explained in chapter 14, suggests that for the purpose of a lower bound, H_{f}

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could be substituted by the classical field energy stored in the A-field, i.e. by

$$E_{\text{magn}} = \frac{1}{2}\int \mathrm{d}^3x\, B(x)^2\,. \tag{20.32}$$

If it could be established that $H_{\text{f}} - E_{\text{magn}} \geq 0$, then

$$H = H + E_{\text{magn}} - E_{\text{magn}} \geq \sum_{j=1}^{N} \frac{1}{2}\big(\sigma_j \cdot (p_j - eA_\varphi(x_j))\big)^2 + V_{\text{coul}} + E_{\text{magn}}\,. \tag{20.33}$$

H-stability of the Coulomb Hamiltonian with magnetic field energy added would have to be shown for an *arbitrary* external transverse vector potential.

To progress towards our goal we note that, for an arbitrary operator A, $|\langle\psi, A^2\psi\rangle| \leq \|A^*\psi\|\,\|A\psi\| \leq \frac{1}{2}\langle\psi, (AA^* + A^*A)\psi\rangle$ and therefore

$$(A + A^*)^2 \leq 2(AA^* + A^*A)\,. \tag{20.34}$$

We split the magnetic field as $B_\varphi(x) = B_\varphi^+(x) + B_\varphi^-(x)$ and apply (20.34),

$$B_\varphi(x)^2 \leq 4B_\varphi^+(x)B_\varphi^-(x) + 2[B_\varphi^+(x), B_\varphi^-(x)]\,, \tag{20.35}$$

which remains true when multiplied by $f(x) \geq 0$. Then

$$\frac{1}{2}\int \mathrm{d}^3x f(x) B_\varphi(x)^2 \leq \|f\|_\infty \sum_{\lambda=1,2} \int \mathrm{d}^3k (2\pi)^3 |\widehat{\varphi}(k)|^2 |k| a^*(k,\lambda) a(k,\lambda)$$
$$+ \|f\|_1 \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 |k|\,. \tag{20.36}$$

Let us assume that $|\widehat{\varphi}(k)| \leq (2\pi)^{-3/2}$ and $\int \mathrm{d}^3k |\widehat{\varphi}(k)|\,|k| = C_\Lambda < \infty$. For f we choose $f(x) = 1$ if $|x - r_j| \leq 1$ for some j and $f(x) = 0$ otherwise. Then

$$H \geq \sum_{j=1}^{N} \frac{1}{2}\big(\sigma_j \cdot (p_j - eA_\varphi(x_j))\big)^2 + V_{\text{coul}} + \frac{1}{2}\int \mathrm{d}^3x f(x) B(x)^2 - KC_\Lambda\,. \tag{20.37}$$

The energy stability with an arbitrary external B-field is difficult, but has been done. Unfortunately the field energy balances the Coulomb attraction only for $|e|$ sufficiently small. To have H-stability for all e one also has to include the B-field gradients. In addition, the choice of f should be optimized. As one result we state

Theorem 20.6 (H-stability of nonrelativistic QED). *Let $\widehat{\varphi}$ be the form factor with sharp cutoff at Λ. Then there exists a positive constant $C(e, Z)$ such that*

$$H \geq -C(e, Z)(\Lambda + 1)K \tag{20.38}$$

independently of N.

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The proof of Theorem 20.6 relies on the H-stability of the Hamiltonian on the right hand side of (20.37) and thus requires the electrons to be fermions.

In the Pauli–Fierz Hamiltonian (20.7) the self-energy of the electrons is not subtracted. Thus, in principle, the stability bound (20.38) could exclusively be due to the positive contribution from the self-energy. To rule out such an unphysical mechanism we employ a technique, briefly touched upon already in section 19.3. The results available are sharper in the case of spinless electrons with Hamiltonian

$$H_N = \sum_{j=1}^{N} \frac{1}{2}\big(p_j - eA_\varphi(x_j)\big)^2 + H_{\rm f} + V_{\rm coul} = T_N + H_{\rm f} + V_{\rm coul}\,. \tag{20.39}$$

Since N is the important parameter, it is displayed explicitly. The no-cutoff Coulomb potential carries the information on the K nuclei located at $r_1, \ldots, r_K$. Let $E(N)$ be the bottom of the spectrum of H_N and $E_0(N)$ that of $T_N + H_{\rm f}$. The binding energy for H_N is defined as in (20.10) with the nucleon repulsion as an additive constant. Then, using (20.11) and assuming $E^0(N) = E_0(N)$,

$$E_{\rm bin}(N) \le E_0(N) - E(N)\,. \tag{20.40}$$

Similar to (19.95) the Coulomb energy is bounded from below as

$$V_{\rm coul} \ge -\kappa e^2 \sum_{j=1}^{N} |p_j - eA_\varphi(x_j)| \tag{20.41}$$

with $\kappa = \big((\pi/2)Z + (2.22)Z^{2/3} + 1.03\big)/4\pi$. Therefore, using Schwarz's inequality,

$$H_N \ge T_N + H_{\rm f} - \kappa e^2 \sqrt{2N}\sqrt{T_N + H_{\rm f}}\,. \tag{20.42}$$

The function $f(x) = x - \kappa e^2\sqrt{2N}\sqrt{x}$ takes its minimum at $x_{\min} = \frac{1}{2}(\kappa e^2)^2 N$, $f(x_{\min}) = -\frac{1}{2}(\kappa e^2)^2 N$. Thus, if

$$E_0(N) \;\le\; \frac{1}{2} N(\kappa e^2)^2 \quad \text{(case I)}\,, \tag{20.43}$$

then $H_N \ge -\frac{1}{2}(\kappa e^2)^2 N$ and $E(N) - E_0(N) \ge -(\kappa e^2)^2 N$. On the other hand, if

$$E_0(N) \;\ge\; \frac{1}{2} N(\kappa e^2)^2 \quad \text{(case II)}\,, \tag{20.44}$$

we can use the fact that f is monotonically increasing to conclude that $H_N \ge f(E_0(N))$ and $E(N) \ge E_0(N) - (e^2\kappa)\sqrt{2N}\sqrt{E_0(N)}$. We summarize as

Theorem 20.7 (Upper bound for N-particle binding energy). *For the Hamiltonian H_N of (20.39), in case I*

$$E_{\rm bin}(N) \le (\kappa e^2)^2 N \tag{20.45}$$

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and in case II

$$E_{\text{bin}}(N) \leq (\kappa e^2)\sqrt{2N}\sqrt{E_0(N)}\,. \tag{20.46}$$

Note that energies are in units of mc^2.

The bound (20.46) is unexpected, since the binding energy is estimated in terms of the self-energy of a system of N electrons without Coulomb repulsion. The Pauli exclusion principle has not yet been invoked.

To make further progress one needs a good estimate on $E_0(N)$. Fermions like to stay alone and the state of lowest energy should be achieved once they are infinitely separated.

Conjecture 20.8 *For fermions*

$$E_0(N) = NE_0(1)\,. \tag{20.47}$$

If Conjecture 20.8 is assumed to hold, then the condition for the two cases reads

$$\text{(case I)}: \quad E_0(1) \leq \frac{1}{2}(\kappa e^2)^2, \quad \text{(case II)}: \quad E_0(1) \geq \frac{1}{2}(\kappa e^2)^2\,. \tag{20.48}$$

As explained in section 19.3, $E_0(1) \leq c_2 e^{4/7}(\Lambda\lambda_{\text{c}})^{12/7}$. Consequently

$$\begin{aligned} E_{\text{bin}} &\leq (\kappa e^2)^2 N && \text{(case I)}\,, \\ E_{\text{bin}} &\leq (\kappa e^2)\sqrt{2c_2}e^{2/7}(\Lambda\lambda_{\text{c}})^{6/7}N && \text{(case II)}\,. \end{aligned} \tag{20.49}$$

The binding energy is extensive. However, our estimate on the stability bound diverges with the cutoff Λ. Since energies are calibrated in units of mc^2, the folklore tells us that multiplying the true stability constant by m/m_{eff} should result in a Λ-independent prefactor.

Notes and references

Stability for the Coulomb Hamiltonian is covered extensively and excellently in survey articles. Particularly recommended are Lieb (1976, 1990), which have become classics. Some of the original articles are reprinted in the Lieb Selecta (2001), where the reader should in addition consult the introduction by Thirring, see also Thirring (2002). The first proof of stability is Dyson and Lenard (1968). The use of the Thomas–Fermi theory as a comparison standard is introduced in Lieb and Thirring (1975). Extensions to Coulomb systems with relativistic kinetic energy are investigated by Conlon (1984), Feffermann and de la Llave (1986), and were finally settled in Lieb and Yau (1988a, b). The basic discovery is that stability holds only under a smallness condition on $Z\alpha$ and α. If electrons were bosons, they would cluster with a density increasing with N. In the ground state energy this can be seen in a faster than linear decrease with N. For bosons and fixed

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nuclei it is known that $E_N \simeq -N^{5/3}$ (Lieb 1979 and references therein), while with bosonic nuclei of finite mass, $E_N \cong -N^{7/5}$ (Dyson 1967; Conlon, Lieb and Yau 1988).

Thermodynamic stability for Coulomb systems is proved by Lieb and Lebowitz (1972).

If photons were scalar, then the Coulomb potential has the "wrong" sign; see section 19.2. This leads to instability, some partial aspects of which are studied in Gallavotti, Ginibre and Velo (1970).

Section 20.1

For Schrödinger operators, $\mathcal{F} = \mathbb{C}$, the exponential localization of Proposition 20.2 goes back to Agmon (1982). Griesemer (2004) observes that it remains valid for general $\mathcal{F}$. Theorem 20.4 is proved by Lieb and Loss (2003). For the helium atom, $N = 2$, the strict positivity of the binding energy is established by Barbaroux *et al.* (2003).

Section 20.2

For the Nelson model, i.e. a scalar Bose field, the limit $c \to \infty$ is studied by Davies (1979), see also Hiroshima (1997a), and the limit $m \to \infty$ by Teufel (2002). They prove that the dynamics is well-approximated through the Coulomb Hamiltonian. Our observation seems to be new, but could have been made already by Davies, if he had chosen the Gross-transformed Nelson Hamiltonian as a starting point.

Section 20.3

The argument leading to Theorem 20.6 is taken from Fefferman, Fröhlich and Graf (1997), see also Bugliaro, Fröhlich and Graf (1996). The harder part is to establish stability for the Hamiltonian on the right hand side of (20.37), which is achieved by Feffermann (1996) with a "sufficiently small" constant and is subsequently improved and simplified by Lieb, Loss and Solovej (1995) to include the physical case. Theorem 20.7 is a result by Lieb and Loss (2002). They also establish that the self-energy for N electrons is bounded as $c_1\alpha^{1/2}(\Lambda\lambda_c)^{3/2}N \leq E_0(N) \leq c_2\alpha^{2/7}(\Lambda\lambda_c)^{12/7}N$ with suitable constants c_1, c_2, which is somewhat weaker than our Conjecture 20.8. The discussion does not change; only the prefactors are less sharp. For bosons the bounds $c_3\alpha^{1/2}(\Lambda\lambda_c)^{3/2}N^{1/2} \leq E_0(N) \leq c_4\alpha^{2/7}(\Lambda\lambda_c)^{12/7}N^{5/7}$ are available, which together with Theorem 20.7 strongly indicate that, as to be expected, bosons remain unstable when the quantized radiation field is added. The basic inequality (20.41) holds also in the case where the electron spin is included, see Lieb and Loss (2002).