Passage from quantum to classical molecular dynamics in the presence of Coulomb interactions

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Abstract

We present a rigorous derivation of classical molecular dynamics (MD) from quantum molecular dynamics (QMD) that applies to the standard Hamiltonians of molecular physics with Coulomb interactions. The derivation is valid away from possible electronic eigenvalue crossings.

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1 Introduction

A basic mathematical formulation of the passage from quantum to classical mechanics, following the ideas of Eugene Wigner [Wig32], is due to Lions and Paul [LP93] and Gérard [Ger91a]: if $\{\Psi_\epsilon\}$ is a sequence of solutions to a semiclassically scaled Schrödinger equation with smooth potential, then the sequence of corresponding Wigner transforms converges (up to subsequences) to a solution of the Liouville equation, i.e. the transport equation of the underlying classical dynamics. For a closely related mathematical approach to semiclassical limits, which goes back to Egorov and is based on Weyl quantization and Moyal calculus, see e.g. [Rob87, Mar02].

Due to the reliance on smooth potentials, and in particular on the existence and uniqueness of trajectories of the classical dynamics, these results are not directly applicable when one tries to derive classical molecular dynamics (MD) from Born-Oppenheimer quantum molecular dynamics (QMD). By the latter, one means quantum dynamics of the molecule's atomic nuclei in the exact non-relativistic Born-Oppenheimer potential energy surface given by the ground state eigenvalue of the electronic Hamiltonian with Coulomb interactions. The limit where the natural small parameter in QMD, the ratio of electronic to nuclear mass $m_e/m_n =: \epsilon^2$, tends to zero, has the structure of a semiclassical limit. (The physical value of this parameter is $\sim 1/2000$ for hydrogen, and even less for the other atoms.) However, the potential energy surface of QMD is not even continuous, because it always contains Coulomb singularities due to nuclei-nuclei repulsion; in addition it can have cone-type singularities at electronic eigenvalue crossings.

Here we present a rigorous derivation of MD from QMD in the limit of small mass ratio that is applicable to the exact Born-Oppenheimer potential energy surface with Coulomb interactions. Our result is valid away from eigenvalue crossings. This is done by extending the approach of Lions and Paul [LP93] to an appropriate class of non-smooth potentials. The

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main technical novelty is a non-concentration estimate on the set of Coulomb singularities, which allows to show, in particular, that the singular term ∇U which appears in the Liouville equation lies in L^1 with respect to the limiting Wigner measure, thereby guaranteeing that the weak formulation of the Liouville equation continues to make sense.

Our methods do not seem to allow to analyse the limit dynamics at eigenvalue crossings, since no analogon of our Coulombic non-concentration estimate is available. In fact, the physically correct starting point to investigate what happens at crossings would not be QMD, as the Born-Oppenheimer approximation underlying QMD also breaks down (see [NW29, Zen32] for earliest insights, [Hag94] for a first rigorous account, and e.g. [FG02, CdV03, Las04, LT05] for recent results).

In the remainder of this Introduction we describe our main result precisely.

Quantum molecular dynamics To simplify matters we assume that all nuclei have equal mass. In atomic units ($m_e = |e| = \hbar = 1$), non-relativistic Born-Oppenheimer quantum molecular dynamics is given by the time-dependent Schrödinger equation

$$\begin{cases} i\epsilon\partial_t\Psi_\epsilon(\cdot,t) = H_\epsilon\Psi_\epsilon(\cdot,t) & \text{for } t\in\mathbb{R}, \\ \Psi_\epsilon(\cdot,0) = \Psi_\epsilon^0, \end{cases} \tag{SE}$$

with Hamiltonian

$$H_\epsilon = -\frac{\epsilon^2}{2}\Delta + U, \tag{1}$$

where $\Psi_\epsilon(\cdot,t)\in L^2(\mathbb{R}^d;\mathbb{C})$ is the wavefunction of the nuclei at time t, $d = 3M$ (M = number of nuclei), Δ is the Laplacian on $\mathbb{R}^d$, $\epsilon := (m_e/m_n)^{1/2}$ is the (dimensionless) small parameter already discussed above (where we have assumed for simplicity that all nuclei have equal mass), and $U : \mathbb{R}^d \to \mathbb{R}$ is the Born-Oppenheimer ground state potential energy surface obtained by minimization over electronic states (see e.g. [SO93]). The precise definition of U is as follows. Let $Z_1, .., Z_M \in \mathbb{N}$ and $R_1, .., R_M \in \mathbb{R}^3$ denote the charges and positions of the nuclei, and let N denote the number of electrons in the system (usually $N = \sum_{\alpha=1}^M Z_\alpha$). Then for $x = (R_1, \ldots, R_M) \in \mathbb{R}^d$

$$U = E_{e\ell} + V_{nn}, \qquad E_{e\ell}(x) = \inf_\psi \langle\psi, H_{e\ell}(x)\psi\rangle, \tag{2}$$

$$V_{nn}(x) = \sum_{1\le\alpha<\beta\le M} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}, \qquad H_{e\ell}(x) = \sum_{i=1}^N \Big(-\frac{1}{2}\Delta_{r_i} - \sum_{\alpha=1}^M \frac{Z_\alpha}{|r_i - R_\alpha|}\Big) + \sum_{1\le i<j\le N} \frac{1}{|r_i - r_j|}.$$

Here the $r_i \in \mathbb{R}^3$ denote electronic coordinates and the infimum is taken over the usual subset of $L^2((\mathbb{R}^3\times\mathbb{Z}_2)^N;\mathbb{C})$ of normalized, antisymmetric electronic states belonging to the domain $H^2((\mathbb{R}^3\times\mathbb{Z}_2)^N;\mathbb{C})$ of $H_{e\ell}(x)$. Physically, $E_{e\ell}$ is the electronic part of the energy, consisting of kinetic energy of the electrons, electron-nuclei attraction, and electron repulsion; this part depends indirectly on the positions R_α of the nuclei since these appear as parameters in the electronic Hamiltonian, and can be shown to be bounded and globally Lipschitz (cf. [FriXX]) although it is not elementary to see this. In case $N \le \sum_{\alpha=1}^M Z_\alpha$, Zhislin's theorem (see [Fri03] for a short proof) says that the infimum in (2) is actually attained, the minimum value being an isolated eigenvalue of finite multiplicity of $H_{e\ell}$. V_{nn} is the direct electrostatic interaction energy between the nuclei, and is the origin of the discontinuities of U.

We remark that quantum molecular dynamics (SE), (1), (2), which is taken as starting point here, itself already constitutes an approximation to full Schrödinger dynamics for electrons and nuclei. Its rigorous justification constitutes an interesting problem in its own right; for a comprehensive treatment in the case of smooth interactions and absence of electronic eigenvalue crossings see [Teu03, PST03].

The potential (2) satisfies the standard Kato-type condition

$$U = U_b + U_s, \quad U_b \in \mathrm{L}^\infty(\mathbb{R}^d), \quad U_s(x) = \sum_{1\le\alpha<\beta\le M} V_{\alpha\beta}(R_\alpha - R_\beta), \quad V_{\alpha\beta} \in \mathrm{L}^2(\mathbb{R}^3) + \mathrm{L}^\infty(\mathbb{R}^3). \quad (3)$$

For such potentials, the operator H_ϵ is self-adjoint on $\mathrm{L}^2(\mathbb{R}^d)$ with domain $\mathcal{D}(H_\epsilon) = \mathrm{H}^2(\mathbb{R}^d)$, cf. [Kat51]. By standard results on the unitary group generated by a self-adjoint operator, for any initial state $\Psi_\epsilon^0 \in \mathcal{D}(H_\epsilon)$ this equation has a unique solution $\Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{H}^2(\mathbb{R}^d)) \cap \mathrm{C}^1(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$, the solution operator $U_\epsilon(t) : \Psi_\epsilon^0 \mapsto \Psi_\epsilon(\cdot, t)$ being unitary. In particular,

$$\|\Psi_\epsilon(\cdot, t)\| = \|\Psi_\epsilon^0\| \text{ for all } t \in \mathbb{R}, \quad (4)$$

where here and below $\|\cdot\|$ denotes the $\mathrm{L}^2(\mathbb{R}^d)$ norm.

The Wigner picture Given the state $\Psi_\epsilon(\cdot, t) \in \mathrm{L}^2(\mathbb{R}^d; \mathbb{C})$ of the system at time t, define the associated Wigner function of lengthscale ϵ on $\mathbb{R}^d \times \mathbb{R}^d$,

$$\begin{aligned} W_\epsilon(x, p, t) &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} e^{-ip\cdot y} \,\mathrm{d}y \\ &= \frac{1}{(2\pi\epsilon)^d} \int_{\mathbb{R}^d} \Psi_\epsilon(x + \frac{y}{2}, t) \overline{\Psi_\epsilon(x - \frac{y}{2}, t)} e^{-ip\cdot y/\epsilon} \,\mathrm{d}y. \end{aligned} \quad (5)$$

Note that the integrand belongs to $\mathrm{L}^1(\mathbb{R}^d_y)$, so W_ϵ is well defined for a.e. $x \in \mathbb{R}^d$. In fact, the integrand is continuous in x with respect to the $\mathrm{L}^1(\mathbb{R}^d_y)$-norm, and hence W_ϵ is continuous in x. Roughly speaking, W_ϵ is a joint position and momentum density of the system. Warning: W_ϵ is not nonnegative except in the limit $\epsilon \to 0$, but at least its marginals are,

$$\begin{aligned} \int_{\mathbb{R}^d} W_\epsilon(x, p, t) \,\mathrm{d}p &= \Big|\Psi_\epsilon(x, t)\Big|^2 \text{ (position density)}, \\ \int_{\mathbb{R}^d} W_\epsilon(x, p, t) \,\mathrm{d}x &= \Big| \underbrace{\frac{1}{(2\pi\epsilon)^{d/2}} \int_{\mathbb{R}^d} e^{-ip\cdot x/\epsilon} \Psi_\epsilon(x, t) \,\mathrm{d}x}_{=:(\mathcal{F}\Psi_\epsilon)(p/\epsilon, t)} \Big|^2 \text{ (momentum density)}. \end{aligned} \quad (6)$$

Here and below, $\mathcal{F}\phi$ denotes the (standard, not scaled) Fourier transform of the function ϕ.

When Ψ_ϵ satisfies (SE), its Wigner function satisfies

$$\begin{aligned} &\partial_t W_\epsilon = -p \cdot \nabla_x W_\epsilon + f_\epsilon, \\ &f_\epsilon(x, p, t) = -\frac{i}{(2\pi)^d} \int_{\mathbb{R}^d} \frac{U(x + \frac{\epsilon y}{2}) - U(x - \frac{\epsilon y}{2})}{\epsilon} \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} e^{-ip\cdot y} \,\mathrm{d}y. \end{aligned} \quad \text{(WE)}$$

Formally, this follows from a lengthy but elementary calculation which goes back to Wigner, see Section 2 below. In this section we also introduce a suitable function space setting in which the calculation becomes rigorous for general self-adjoint Hamiltonians of type (1). We call eq. (WE) the *Wigner equation*. Note that it contains no modification of quantum dynamics (SE), but is just a different mathematical formulation of it.

Limit dynamics ¿From now on we focus on the specific potential energy surface (2). In the limit $\epsilon \to 0$, the difference quotient in the potential term satisfies

$$\frac{U(x + \frac{\epsilon y}{2}) - U(x - \frac{\epsilon y}{2})}{\epsilon} \to \nabla U(x) \cdot y \quad \text{a.e.}$$

(due to the Lipschitz continuity of $E_{e\ell}$ and the fact that the singular set of V_{nn} is of measure zero). To understand what happens with eq. (WE) in the limit, it is useful to split f_ϵ into a term containing $\nabla U(x) \cdot y$ and a term containing the difference quotient of U minus its limit. The first term simplifies due to $ye^{-ip\cdot y} = i\nabla_p e^{-ip\cdot y}$, giving

$$f_\epsilon = \nabla U(x) \cdot \nabla_p W_\epsilon + g_\epsilon,$$

where

$$g_\epsilon = -\frac{i}{(2\pi)^d} \int_{\mathbb{R}^d} \Big[\frac{U(x+\frac{\epsilon y}{2}) - U(x - \frac{\epsilon y}{2})}{\epsilon} - \nabla U(x) \cdot y \Big] \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} e^{-ip\cdot y} \, \mathrm{d}y.$$

Formally, passing to the limit in (WE) and assuming that g_ϵ tends to zero, we obtain the *Liouville equation*

$$\partial_t W = -p \cdot \nabla_x W + \nabla U(x) \cdot \nabla_p W. \qquad \text{(LE)}$$

This is the transport equation for classical molecular dynamics in $\mathbb{R}^d \times \mathbb{R}^d$ with potential U,

$$\dot{x} = p, \quad \dot{p} = -\nabla U(x). \qquad \text{(MD)}$$

Moreover, assuming the initial data to (SE) to be normalized, by (6) one expects $\int_{\mathbb{R}^{2d}} \mathrm{d}W(t) = 1$, i.e. $W(t)$ should be a probability measure on phase space for all $t \in \mathbb{R}$.

The main difficulties in making this rigorous for rough potentials lie in (a) justifying the existence of a limiting probability measure on phase space for all times and general initial data which are not restricted to 'avoid' the singularities, (b) justifying that g_ϵ goes to zero. The latter issue arises because when the potential U is not everywhere differentiable, the term in square brackets does not go to zero for every x, let alone locally uniformly. On the other hand, the remaining part of the integrand can concentrate on individual positions x when standard semiclassical wave packets such as

$$\Psi_\epsilon^0(x) = \epsilon^{-\frac{\alpha d}{2}} e^{i\frac{p_0}{\epsilon}\cdot x} \phi(\tfrac{x - x_0}{\epsilon^\alpha}), \quad 0 < \alpha < 1, \quad \|\phi\| = 1,$$

are under consideration, whose Wigner function converges to $\delta_{(x_0,p_0)}$. Thus the only viable strategy appears to be to establish that the Wigner function does not charge the singular set in the limit.

Main result Our rigorous result achieves goal (a) in the desired generality, and goal (b) away from possible crossings, establishing in particular that the Liouville equation (LE) remains valid across Coulomb singularities. In order to formulate our result we need the following definition.

Definition 1.1 *A sequence $\{\mu_\epsilon\}$ of nonnegative Radon measures on $\mathbb{R}^d$ is called* tight *if*

$$\lim_{R\to\infty} \limsup_{\epsilon \to 0} \int_{|x|>R} \mathrm{d}\mu_\epsilon = 0.$$

Theorem 1.1 *Suppose $U : \mathbb{R}^d \to \mathbb{R}$ is the Born-Oppenheimer potential energy surface (2) of any molecule, or more generally $U = U_b + U_s$ with $U_b \in \mathrm{W}^{1,\infty}(\mathbb{R}^d)$,*

$$U_s(x) = \sum_{1\le\alpha<\beta\le M} \frac{C_{\alpha\beta}}{|R_\alpha - R_\beta|}, \quad C_{\alpha\beta} \ge 0, \quad x = (R_1, \ldots, R_M) \in \mathbb{R}^d. \qquad (7)$$

Let $\{\Psi_\epsilon^0\}_{\epsilon>0}$ be a sequence of initial data such that $\Psi_\epsilon \in \mathrm{H}^2(\mathbb{R}^d)$, $\|\Psi_\epsilon^0\| = 1$, $\|H_\epsilon \Psi_\epsilon^0\| \le c$ for some constant c independent of ϵ, $\{|\Psi_\epsilon^0|^2\}$ tight. Let $\Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{H}^2(\mathbb{R}^d)) \cap \mathrm{C}^1(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$ be the *corresponding solutions to the time-dependent Schrödinger equation* (SE)*, and let* W_ϵ *be their Wigner transforms* (5)*. Then:*

(i) (Compactness) For a subsequence, $W_\epsilon \rightharpoonup W$ *in* $\mathcal{D}'(\mathbb{R}^{2d+1})$*.*

(ii) (Existence of a limiting probability measure on phase space) $W \in \mathrm{C}_{weak*}(\mathbb{R}; \mathcal{M}(\mathbb{R}^{2d}))$*, and* $W(t)$ *is a probability measure for all* t*, that is to say* $W(t) \geq 0$ *and* $\int_{\mathbb{R}^{2d}} \mathrm{d}W(t) = 1$*.*

(iii) (No-concentration estimate at Coulomb singularities) For all t *we have* $\nabla U_s \in \mathrm{L}^1(\mathrm{d}W(t))$*, and* $W(t)(\mathcal{S} \times \mathbb{R}^d) = 0$*, where* $\mathcal{S}$ *is the singular set* $\{x = (R_1, \ldots, R_M) \in \mathbb{R}^{3M} \mid R_\alpha = R_\beta$ *for some* $\alpha \neq \beta$ *with* $C_{\alpha\beta} \neq 0\}$*.*

(iv) (Limit equation) If $\Omega \subseteq \mathbb{R}^d$ *is any open set such that* $U_b \in \mathrm{C}^1(\Omega)$*, then* W *is a global weak solution of the Liouville equation* (LE) *on* $\Omega \times \mathbb{R}^d \times \mathbb{R}$*, that is to say*

$$\int_{\mathbb{R}} \int_{\mathbb{R}^{2d}} \Big(\partial_t + p \cdot \nabla_x - \nabla U(x) \cdot \nabla_p\Big) \phi(x,p,t) \, \mathrm{d}W(t) \, \mathrm{d}t = 0 \tag{8}$$

for all $\phi \in \mathrm{C}_0^\infty(\Omega \times \mathbb{R}^d \times \mathbb{R})$*.*

Remarks 1) The regularity requirement $U_b \in \mathrm{C}^1$ in (iv) is minimal in order for the weak Liouville equation (8) to make sense for general measure valued solutions W. This is due to the appearance of ∇U inside the integral with respect to the measure $\mathrm{d}W(t)$. Note however that in case of (2) this narrowly excludes eigenvalue crossings, as seen from the 2D matrix example

$$H_{e\ell} = \begin{pmatrix} \rho_1 & -\rho_2 \\ \rho_2 & \rho_1 \end{pmatrix},$$

whose ground state eigenvalue equals $-|\rho|$, and is hence Lipschitz but not C^1. For interesting model problems with scalar or vector-valued potentials in which the behaviour of Wigner measures past discontinuities of ∇U can be analysed for suitable classes of initial data see [Ker05] and [FG02, Las04, LT05].

2) The assumptions on the potential U are far weaker than those needed for uniqueness of the Hamiltonian ODE (MD) underlying the limit equation. Recall that the standard condition guaranteeing uniqueness for ODE's $\dot{z} = f(z)$ is boundedness of the gradient of the vector field f, which in the case of (MD) means boundedness of the *second*, not the first gradient of U. Our assumptions on U are also weaker than those under which uniqueness for weak (L^p) solutions to (LE) is known. The recent nontrivial uniqueness results for transport equations ([Amb04]) require $f \in \mathrm{BV}$, i.e. in case of (MD), $\nabla U \in \mathrm{BV}$ (for recent refinements see [BC09], [AGS08]). Interestingly, however, the latter requirement, while violated by the Coulombic part $U_s = V_{nn}$ in (2), would be met by the model eigenvalue crossing in Remark 1), and expected to be met by the electronic part $U_b = E_{e\ell}$ in (2). We hope to address uniqueness in future work.

3) The higher integrability result in (iii) that $\nabla U_s \in \mathrm{L}^1(\mathrm{d}W(t))$, which is essential for making sense of the limit equation at Coulomb singularities, requires a quantitative no-concentration estimate of form

$$\int_{|R_\alpha - R_\beta| < \delta} \mathrm{d}W(t) = O(\delta^2) \text{ as } \delta \to 0, \tag{9}$$

for any $\alpha \neq \beta$ with $C_{\alpha\beta} \neq 0$. This is because $|\nabla_{R_\alpha}(1/|R_\alpha - R_\beta|)| = 1/|R_\alpha - R_\beta|^2 \geq 1/\delta^2$ in $|R_\alpha - R_\beta| < \delta$. We do not think that the validity of such an estimate is obvious, the naively expected bound only being $O(\delta)$ instead of $O(\delta^2)$ (on grounds of the potential energy term $\int U_s |\Psi_\epsilon|^2$, which can be controlled independently of ϵ and t by energy conservation, only containing the weaker singularities $1/|R_\alpha - R_\beta|$). See Sections 4 and 5 for the proof of (9).

4) In the special case $U_s = 0$, $U_b \in \mathrm{W}^{2,\infty}(\mathbb{R}^d)$, (iv) holds with $\Omega = \mathbb{R}^d$, so Theorem 1.1 recovers the result of Lions and Paul [LP93, Théorème IV.1.1)].

5) In the special case of the potential energy surface (2) of the H_2 molecule ($M = 2$, $N = 2$, $Z_1 = Z_2 = 1$), it is known that the ground state eigenvalue of the electronic Hamiltonian is nondegenerate. It then follows from a result of Hunziker [Hun86] that U_b is analytic, and in particular C^1, on $\Omega = \mathbb{R}^6 \backslash \mathcal{S}$, and Theorem 1.1 justifies classical molecular dynamics globally.

6) Also, more can be said about the set Ω in (iv) in the case of the potential energy surface (2) of a general neutral or positively charged dimer ($M = 2$, $N \le Z_1 + Z_2$). By invariance of the electronic Hamiltonian $H_{e\ell}$ and the nuclei-nuclei interaction V_{nn} in (2) under simultaneous rotation and translation of all particles, we have that $U(R_1, R_2) = u(|R_1 - R_2|)$, that is to say the potential is a function of a single parameter, internuclear distance. It then follows by combining the result of Hunziker [Hun86] with a classical result of Kato on analyticity of eigenvalues of analytic one-parameter families of Hamiltonians [Kat95] that we may take $\Omega = \mathbb{R}^6 \backslash (\mathcal{S} \cup \mathcal{C})$, where $\mathcal{S} = \{R_1 = R_2\}$ is the set of Coulomb singularities introduced in part (iii) of the theorem, and $\mathcal{C} = \bigcup_j \{|R_1 - R_2| = c_j\}$, the c_j being the (possibly empty) discrete subset of $\mathbb{R}^+$ of interatomic distances at which the lowest two eigenvalues of the electronic Hamiltonian cross. Note in particular that $\mathcal{S} \cup \mathcal{C}$ is a closed set of measure zero; hence Theorem 1.1 justifies the Liouville equation on an open set of full measure. We expect that when U is given by (2), it is always smooth on an open set of full measure. Note however that such a result does not follow solely from consideration of non-degenerate eigenvalues as in [Hun86].

7) As shown below (Lemma 3.2), the weak convergence in (i) also holds in the stronger spaces $\mathrm{L}^\infty_{weak*}(\mathbb{R}; \mathcal{A}')$ and $\mathrm{C}_{weak*,loc}(\mathbb{R}; \mathcal{A}')$, with $\mathcal{A}$ being the Banach space defined in (16).

2 Wigner-transformed quantum dynamics

We now make precise in an appropriate function space setting the well known fact (discussed informally in the Introduction) that the Wigner transform takes solutions of the Schrödinger equation (SE) to solutions of the Wigner equation (WE). Our choice of spaces is convenient for our goal to study the limit dynamics for rough potentials. In other contexts other function spaces have been considered [Mar89].

We begin with the well known formal derivation (assuming that the wavefunction is smooth and rapidly decaying for all t).

Formal derivation Let Ψ_ϵ be a solution to (SE), and let W_ϵ denote its Wigner transform (5). Differentiating the latter with respect to t, we obtain

$$\partial_t W_\epsilon(x,p,t) = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \Big[\big(\partial_t \Psi_\epsilon(x + \frac{\epsilon y}{2}, t)\big) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} + \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\partial_t \Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} \Big] e^{-ip\cdot y}\, \mathrm{d}y. \tag{10}$$

By (SE) and $\Delta_{\pm\epsilon y/2} = (4/\epsilon^2)\Delta_y$ this is equivalent to

$$\begin{aligned} \partial_t W_\epsilon(x,p,t) &= f_\epsilon(x,p,t) \\ &+ \frac{2i}{\epsilon(2\pi)^d} \int_{\mathbb{R}^d} \Big[\big(\Delta_y \Psi_\epsilon(x + \frac{\epsilon y}{2}, t)\big) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} - \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\Delta_y \Psi_\epsilon(x - \frac{\epsilon y}{2}, t)} \Big] e^{-ip\cdot y}\, \mathrm{d}y \end{aligned} \tag{11}$$

with f_ϵ as in (WE). The Laplacian terms can be simplified via the formula $(\Delta a)\bar{b} - a\overline{\Delta b} = \mathrm{div}(\nabla a \cdot \bar{b} - a \cdot \nabla \bar{b})$, an integration by parts, and the formula $\nabla_y = \pm(\epsilon/2)\nabla_{\pm\epsilon y/2}$, whence the integral in (11) becomes

$$\int_{\mathbb{R}^d} \operatorname{div}\Big[\big(\nabla_y \Psi_\epsilon(x+\frac{\epsilon y}{2},t)\big)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)} - \Psi_\epsilon(x+\frac{\epsilon y}{2})\overline{\nabla_y\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}\Big] e^{-ip\cdot y}\,\mathrm{d}y \tag{12}$$

$$= ip\cdot\int_{\mathbb{R}^d}\Big[\big(\nabla_y \Psi_\epsilon(x+\frac{\epsilon y}{2},t)\big)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)} - \Psi_\epsilon(x+\frac{\epsilon y}{2},t)\overline{\nabla_y\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}\Big] e^{-ip\cdot y}\,\mathrm{d}y \tag{13}$$

$$= \frac{\epsilon i}{2}\,p\cdot\int_{\mathbb{R}^d}\nabla_x\Big[\Psi_\epsilon(x+\frac{\epsilon y}{2},t)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}\Big]e^{-ip\cdot y}\,\mathrm{d}y \tag{14}$$

$$= \frac{\epsilon(2\pi)^d}{2i}\big(-p\cdot\nabla_x W_\epsilon(x,p,t)\big).$$

Substituting this expression into (11), we obtain (WE).

Rigorous derivation In the sequel, position coordinates in $\mathbb{R}^d$, $d=3M$, are denoted by $x=(x_1,..,x_d)=(R_1,..,R_M)\in\mathbb{R}^d$, $x_i\in\mathbb{R}$, $R_\alpha\in\mathbb{R}^3$.

Lemma 2.1 *The Wigner transform (5) of any solution $\Psi_\epsilon\in \mathrm{C}(\mathbb{R};\mathrm{H}^2(\mathbb{R}^d))\cap \mathrm{C}^1(\mathbb{R};\mathrm{L}^2(\mathbb{R}^d))$ of the Schrödinger equation* (SE) *with U as in* (3) *satisfies*

$$W_\epsilon\in \mathrm{C}^1(\mathbb{R};\mathrm{L}^\infty(\mathbb{R}^{2d})),\ \frac{\partial}{\partial x_i}W_\epsilon,\ \frac{\partial^2}{\partial x_i\partial x_j}W_\epsilon,\ \textit{and } f_\epsilon\in \mathrm{C}(\mathbb{R};\mathrm{L}^\infty(\mathbb{R}^{2d}))\quad \textit{for all}\quad i,j=1,\dots,d \tag{15}$$

and solves the Wigner equation (WE).

To obtain an effortless proof, the idea is to express all terms under investigation with the help of the following bilinear map which extends the quadratic map $\Psi_\epsilon\mapsto W_\epsilon$ introduced in (5):

$$F_\epsilon(\Psi,\chi) := \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\Psi(x+\tfrac{\epsilon y}{2})\overline{\chi(x-\tfrac{\epsilon y}{2})}e^{-ip\cdot y}\,\mathrm{d}y.$$

Lemma 2.2 *The map $(\Psi,\chi)\mapsto F_\epsilon(\Psi,\chi)$ is a continuous map from $\mathrm{L}^2(\mathbb{R}^d)\times\mathrm{L}^2(\mathbb{R}^d)$ to $\mathrm{L}^\infty(\mathbb{R}^{2d})$. In particular, the map $\Psi_\epsilon\mapsto W_\epsilon=F_\epsilon(\Psi_\epsilon,\Psi_\epsilon)$ is a continuous map from $\mathrm{L}^2(\mathbb{R}^d)$ to $\mathrm{L}^\infty(\mathbb{R}^{2d})$.*

Proof of Lemma 2.2 Let Ψ, Ψ', χ, $\chi'\in\mathrm{L}^2(\mathbb{R}^d)$, $W=F_\epsilon(\Psi,\chi)$, $W'=F_\epsilon(\Psi',\chi')$. Then

$$\begin{aligned}
&|W(x,p)-W'(x,p)|\\
&=\frac{1}{(2\pi)^d}\left|\int_{\mathbb{R}^d}\Big((\Psi-\Psi')(x+\tfrac{\epsilon y}{2})\overline{\chi(x-\tfrac{\epsilon y}{2})}+\Psi'(x+\tfrac{\epsilon y}{2})\overline{(\chi-\chi')(x-\tfrac{\epsilon y}{2})}\Big)e^{-ip\cdot y}\,\mathrm{d}y\right|\\
&\le\frac{1}{(2\pi)^d}\Big(\|(\Psi-\Psi')(x+\tfrac{\epsilon\cdot}{2})\|\,\|\chi(x-\tfrac{\epsilon\cdot}{2})\|+\|\Psi'(x+\tfrac{\epsilon\cdot}{2})\|\,\|(\chi-\chi')(x-\tfrac{\epsilon\cdot}{2})\|\Big)\\
&=\Big(\frac{1}{\epsilon\pi}\Big)^d\Big(\|\Psi-\Psi'\|\,\|\chi\|+\|\Psi'\|\,\|\chi-\chi'\|\Big)
\end{aligned}$$

for all x and p. Taking $\Psi'=\chi'=0$ shows $W\in\mathrm{L}^\infty(\mathbb{R}^{2d})$, and the estimate above establishes the asserted continuity of F_ϵ. □

Proof of Lemma 2.1 First, we claim that $W_\epsilon\in\mathrm{C}(\mathbb{R};\mathrm{L}^\infty(\mathbb{R}^d))$. This is immediate from $\Psi_\epsilon\in\mathrm{C}(\mathbb{R};\mathrm{L}^2(\mathbb{R}^d))$ and Lemma 2.2.

Next, we investigate the terms $\frac{\partial}{\partial x_i}W_\epsilon$, $\frac{\partial^2}{\partial x_i\partial x_j}W_\epsilon$, and f_ϵ. The underlying terms $\frac{\partial}{\partial x_i}\Psi_\epsilon$, $\frac{\partial^2}{\partial x_i\partial x_j}\Psi_\epsilon$ and $U\Psi_\epsilon$ are in $\mathrm{C}(\mathbb{R};\mathrm{L}^2(\mathbb{R}^d))$, because $\Psi_\epsilon\in\mathrm{C}(\mathbb{R};\mathrm{H}^2(\mathbb{R}^d))$ and the operators $\frac{\partial}{\partial x_i}$, $\frac{\partial^2}{\partial x_i\partial x_j}$

and $U = H_\epsilon - \frac{\epsilon^2}{2}\Delta$ are continuous maps from $\mathrm{H}^2(\mathbb{R}^d)$ to $\mathrm{L}^2(\mathbb{R}^d)$. Note now that we have the following representations with the help of the bilinear map F_ϵ:

$$\frac{\partial}{\partial x_i} W_\epsilon = F_\epsilon\Big(\tfrac{\partial}{\partial x_i}\Psi_\epsilon, \Psi_\epsilon\Big) + F_\epsilon\Big(\Psi_\epsilon, \tfrac{\partial}{\partial x_i}\Psi_\epsilon\Big),$$

$$\frac{\partial^2}{\partial x_i \partial x_j} W_\epsilon = F_\epsilon\Big(\tfrac{\partial^2}{\partial x_i \partial x_j}\Psi_\epsilon, \Psi_\epsilon\Big) + F_\epsilon\Big(\tfrac{\partial}{\partial x_i}\Psi_\epsilon, \tfrac{\partial}{\partial x_j}\Psi_\epsilon\Big) + F_\epsilon\Big(\tfrac{\partial}{\partial x_j}\Psi_\epsilon, \tfrac{\partial}{\partial x_i}\Psi_\epsilon\Big) + F_\epsilon\Big(\Psi_\epsilon, \tfrac{\partial^2}{\partial x_i \partial x_j}\Psi_\epsilon\Big),$$

$$f_\epsilon = -\frac{i}{\epsilon}\Big(F_\epsilon(U\Psi_\epsilon, \Psi_\epsilon) - F_\epsilon(\Psi_\epsilon, U\Psi_\epsilon)\Big).$$

It now follows from Lemma 2.2 that these terms are in $\mathrm{C}(\mathbb{R}; \mathrm{L}^\infty(\mathbb{R}^{2d}))$.

It remains to show that $W_\epsilon \in \mathrm{C}^1(\mathbb{R}; \mathrm{L}^\infty(\mathbb{R}^{2d}))$, with derivative $\partial_t W_\epsilon$ given by eq. (WE). First we show continuous differentiability with respect to time. We have

$$\begin{aligned}\frac{W_\epsilon(\cdot, t+h) - W_\epsilon(\cdot, t)}{h} &= \frac{F_\epsilon(\Psi_\epsilon(\cdot, t+h), \Psi_\epsilon(\cdot, t+h)) - F_\epsilon(\Psi_\epsilon(\cdot, t), \Psi_\epsilon(\cdot, t))}{h} \\ &= F_\epsilon\Big(\tfrac{\Psi_\epsilon(\cdot, t+h) - \Psi_\epsilon(\cdot, t)}{h}, \Psi_\epsilon(\cdot, t+h)\Big) + F_\epsilon\Big(\Psi_\epsilon(\cdot, t), \tfrac{\Psi_\epsilon(\cdot, t+h) - \Psi_\epsilon(\cdot, t)}{h}\Big).\end{aligned}$$

Hence by the two convergences $\frac{\Psi_\epsilon(\cdot,t+h)-\Psi_\epsilon(\cdot,t)}{h} \to \partial_t \Psi_\epsilon(\cdot, t)$ in $\mathrm{L}^2(\mathbb{R}^d)$ (from $\Psi_\epsilon \in \mathrm{C}^1(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$) and $\Psi_\epsilon(\cdot, t+h) \to \Psi_\epsilon(\cdot, t)$ in $\mathrm{L}^2(\mathbb{R}^d)$ (from $\Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$) and the continuity of F_ϵ,

$$\frac{W_\epsilon(\cdot, t+h) - W_\epsilon(\cdot, t)}{h} \to F_\epsilon(\partial_t \Psi_\epsilon(\cdot, t), \Psi_\epsilon(\cdot, t)) + F_\epsilon(\Psi_\epsilon(\cdot, t), \partial_t \Psi_\epsilon(\cdot, t)) \text{ in } \mathrm{L}^\infty(\mathbb{R}^{2d}) \text{ as } h \to 0.$$

Consequently $t \mapsto W_\epsilon(\cdot, t)$ is a differentiable map from $\mathbb{R}$ to $\mathrm{L}^\infty(\mathbb{R}^{2d})$, with derivative given by eq. (10). Continuity in time of the derivative $\partial_t W_\epsilon$, i.e. the fact that $W_\epsilon \in \mathrm{C}^1(\mathbb{R}; \mathrm{L}^\infty(\mathbb{R}^{2d}))$, now follows from (10), $\Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$, $\partial_t \Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$, and – one more time – the continuity of F_ϵ (Lemma 2.2).

We conclude the proof by showing that W_ϵ satisfies (WE). The formal derivation of this equation from eq. (10) (which we have already established above) has been performed by the calculations (11)—(14). Here, we need only to justify these calculations rigorously. Eq. (11) follows immediately from (10) and (SE). Note that all four summands of the integrands on the RHS of eq. (11) (cf. also the definition of f_ϵ in (WE)), separately belong to $\mathrm{L}^1(\mathbb{R}^d_y)$, for any x, p and t, because $U(x \pm \frac{\epsilon y}{2})\Psi_\epsilon(x \pm \frac{\epsilon y}{2}, t)$ and $\Delta_x \Psi_\epsilon(x \pm \frac{\epsilon y}{2}, t)$ belong to $\mathrm{L}^2(\mathbb{R}^d_y)$. Eq. (12) follows from the product rule for the Laplacian, and eq. (13) from the fact that the vector field inside the square brackets of (12) belongs to the Sobolev space $\mathrm{W}^{1,1}(\mathbb{R}^d_y) = \mathrm{W}^{1,1}_0(\mathbb{R}^d_y)$ and $e^{-ip\cdot y} \in \mathrm{W}^{1,\infty}(\mathbb{R}^d_y)$, and that $\int_{\mathbb{R}^d} \mathrm{div}(v)\phi = -\int_{\mathbb{R}^d} v \cdot \nabla\phi$ for all $v \in \mathrm{W}^{1,1}_0(\mathbb{R}^d)$, $\phi \in \mathrm{W}^{1,\infty}(\mathbb{R}^d)$. Finally, eq. (14) follows from an elementary change of variables, concluding the proof. □

3 Time-dependent Wigner measures

We first give a modest technical extension of the construction of Wigner measures in [LP93]. Instead of considering a sequence of wavefunctions at a fixed time t, we consider a sequence of continuous paths $\Psi_\epsilon \in \mathrm{C}(\mathbb{R}; \mathrm{L}^2(\mathbb{R}^d))$ – not required to satisfy any equation – and show that under mild conditions these give rise to a continuous path $W \in \mathrm{C}_{weak*}(\mathbb{R}; \mathcal{M}(\mathbb{R}^{2d}))$ of Wigner measures. See Lemma 3.2. We then combine the lemma with careful a priori estimates on the singular contributions to f_ϵ in eq. (WE) and a lemma on propagation of tightness under (SE) to prove Theorem 1.1 (i) and (ii). An interesting feature of these proofs is that, in contrast to the existing literature, they are extracted directly from the Schrödinger dynamics, without relying on a representation of the limit measure as push-forward of its initial data under (MD), which is not available here. As regards our proof in (ii) that $\int_{\mathbb{R}^{2d}} \mathrm{d}W(t) = 1$ for all t, our argument via Schrödinger dynamics is inspired by Corollary 1 in [FL03] (see also Proposition 4 in [Las04]).

We begin by recalling the notion of weak convergence of Wigner transforms at a fixed time t to Wigner measures introduced in [LP93]. For an alternative construction of Wigner measures see [Ger91a]. Closely related constructions are the microlocal defect measures of Gérard [Ger91b], motivated by questions in microlocal analysis, and the H-measures of Tartar [Tar90], motivated by questions in homogenization theory.

Let $\mathcal{A}$ denote the following Banach space

$$\mathcal{A} := \{\phi \in \mathrm{C}_0(\mathbb{R}^{2d}) \mid \|\phi\|_{\mathcal{A}} := \int_{\mathbb{R}^d} \sup_{x\in\mathbb{R}^d} |(\mathcal{F}_p\phi)(x,y)|\,\mathrm{d}y < \infty\}. \tag{16}$$

Here $\mathrm{C}_0(\mathbb{R}^{2d})$ is the usual space of continuous functions on $\mathbb{R}^{2d}$ tending to zero at infinity, and $\mathcal{F}_p\phi$ is the partial Fourier transform $(\mathcal{F}_p\phi)(x,y) = \int_{\mathbb{R}^d} e^{-ip\cdot y}\phi(x,p)\,\mathrm{d}p$. Since $\mathcal{A}$ is a dense subset of $\mathrm{C}_0(\mathbb{R}^{2d})$, its dual $\mathcal{A}'$ contains $\mathrm{C}_0'(\mathbb{R}^{2d}) = \mathcal{M}(\mathbb{R}^{2d})$, the space of not necessarily nonnegative Radon measures on $\mathbb{R}^{2d}$ of finite mass. In particular, the delta function $\delta_{(x_0,p_0)}$ centered at a single point (x_0,p_0) in classical phase space belongs to $\mathcal{A}'$, and weak* convergence in $\mathcal{A}'$ allows convergence of smeared-out Wigner functions coming from a quantum state to a delta function on phase space (i.e., a "classical" state).

The following basic facts were established by Lions and Paul.

Lemma 3.1 *(Wigner measures) [LP93]*
(i) (compactness) Let $\{\Psi_\epsilon\}$ be any sequence in $\mathrm{L}^2(\mathbb{R}^d)$ such that

$$\|\Psi_\epsilon\|^2 \le C \tag{17}$$

for some constant C independent of ϵ. Then the sequence of corresponding Wigner transforms $\{W_\epsilon\}$ contains a subsequence $\{W_{\epsilon'}\}$ converging weak in $\mathcal{A}'$ to some $W \in \mathcal{A}'$.*
(ii) (positivity) Any such limit $W \in \mathcal{A}'$ satisfies $W \in \mathcal{M}(\mathbb{R}^{2d})$, $W \ge 0$. In other words, W is a nonnegative Radon measure of finite mass.
(iii) (upper bound) Let $\{\Psi_{\epsilon'}\}$ be a further subsequence such that $|\Psi_{\epsilon'}|^2 \overset{*}{\rightharpoonup} \mu$ in $\mathcal{M}(\mathbb{R}^d)$. Then

$$\int_{p\in\mathbb{R}^d} W(\cdot,\mathrm{d}p) \le \mu.$$

In particular, any limit W as in (i) satisfies $\int_{\mathbb{R}^{2d}} \mathrm{d}W \le C$, with C as in (17).
(iv) (preservation of mass) If $\|\Psi_\epsilon\|^2 = C$ for all ϵ, and the sequences of position and momentum densities are both tight, that is to say

$$\limsup_{\epsilon\to 0}\int_{|x|>R} |\Psi_\epsilon(x)|^2\,\mathrm{d}x \to 0, \quad \limsup_{\epsilon\to 0}\int_{|p|>R}\left|\frac{1}{(2\pi\epsilon)^{d/2}}(\mathcal{F}\Psi_\epsilon)\left(\frac{p}{\epsilon}\right)\right|^2\mathrm{d}p \to 0 \quad (R\to\infty),$$

then $\displaystyle\int_{\mathbb{R}^{2d}} \mathrm{d}W = C$. In particular, in the case $C = 1$, W is a probability measure.

For future purposes we note that (i) is immediate from the Banach-Alaoglu theorem and the elementary estimate

$$\Big|\int_{\mathbb{R}^{2d}} W_\epsilon \phi \,\mathrm{d}(x,p)\Big| \leq \frac{1}{(2\pi)^d}\|\Psi_\epsilon\|^2\|\phi\|_{\mathcal{A}} \quad \text{for } \phi\in\mathcal{A}, \tag{18}$$

which implies

$$\|W_\epsilon\|_{\mathcal{A}'} = \sup_{\phi\in\mathcal{A}\setminus\{0\}} \frac{\int W_\epsilon\,\phi}{\|\phi\|_{\mathcal{A}}} \leq \frac{1}{(2\pi)^d}\|\Psi_\epsilon\|^2, \tag{19}$$

that is to say $\{W_\epsilon\}$ is a bounded sequence in $\mathcal{A}'$. The proofs of (ii) and (iii) are less elementary, and require use of the Husimi transform; see [LP93].

An analogue yielding time-continuous paths of Wigner measures is the following.

Lemma 3.2 *(Time-dependent Wigner measures)*
(i) (compactness) Let $\{\Psi_\epsilon\}$ be a sequence in $\mathrm{C}(\mathbb{R};\mathrm{L}^2(\mathbb{R}^d))$ such that

$$\sup_{t\in\mathbb{R}} \|\Psi_\epsilon(\cdot,t)\|^2 \leq C \tag{20}$$

for some constant independent of ϵ, and let $\{W_\epsilon\}$ be the sequence of associated Wigner functions. Then for a subsequence, $W_\epsilon \overset{*}{\rightharpoonup} W$ weak in $\mathrm{L}^\infty(\mathbb{R};\mathcal{A}')$.*
(ii) Suppose in addition that for any test function $\phi\in\mathrm{C}_0^\infty(\mathbb{R}^{2d})$ the functions

$$f_{\epsilon,\phi}(t) := \int_{\mathbb{R}^{2d}} W_\epsilon(x,p,t)\,\phi(x,p)\,\mathrm{d}(x,p)$$

are differentiable and satisfy

$$\sup_{t\in\mathbb{R}} |\tfrac{\mathrm{d}}{\mathrm{d}t} f_{\epsilon,\phi}(t)| \leq C_\phi \tag{21}$$

for some constant C_ϕ independent of ϵ. Then, $W\in\mathrm{C}_{weak*}(\mathbb{R};\mathcal{M}(\mathbb{R}^{2d}))$, $W(t)\geq 0$ for all t, and $W_\epsilon(\cdot,t) \overset{*}{\rightharpoonup} W(t)$ in $\mathcal{A}'$ for all t. Moreover, the latter convergence is uniform on compact time intervals, i.e., for any test function $\phi\in\mathcal{A}$ and any compact $I\subset\mathbb{R}$, $f_{\epsilon,\phi}(t)$ converges uniformly with respect to $t\in I$ to $\int_{\mathbb{R}^{2d}}\phi\,\mathrm{d}W(t)$.

Here (i) is a straightforward adaptation of the time-independent theory in [LP93]. The key point is the assertion in (ii) that the limit measure has slightly higher regularity in time than naïvely expected (continuous instead of L^∞). This allows, in particular, to make sense of initial values.

Proof The first part is an easy consequence of Lemma 3.1, cf. (19), and assumption (20), which imply that $\{W_\epsilon\}$ is bounded in $\mathrm{L}^\infty(\mathbb{R};\mathcal{A}')$. Since the latter is the dual of the separable space $\mathrm{L}^1(\mathbb{R};\mathcal{A})$, the assertion follows from the Banach-Alaoglu theorem.

The second part is less trivial, and requires various approximation arguments. First, we test the weak* convergence of $\{W_\epsilon\}$ from (i) against tensor products $\phi(x,p)\chi(t)$ with $\phi\in\mathcal{A}$, $\chi\in\mathrm{L}^1(\mathbb{R})$. This gives

$$\int_{\mathbb{R}} f_{\epsilon,\phi}(t)\chi(t)\,\mathrm{d}t = \int_{\mathbb{R}^{2d+1}} W_\epsilon\,\phi\otimes\chi\,\mathrm{d}(x,p,t) \to \int_{\mathbb{R}}\int_{\mathbb{R}^{2d}} \phi\otimes\chi\,\mathrm{d}W(t)\,\mathrm{d}t = \int_{\mathbb{R}} f_\phi(t)\chi(t)\,\mathrm{d}t,$$

where $f_\phi(t) := \int_{\mathbb{R}^{2d}}\phi\,\mathrm{d}W(t)$. Consequently $f_{\epsilon,\phi} \overset{*}{\rightharpoonup} f_\phi$ in $\mathrm{L}^\infty(\mathbb{R})$.

Now let $\phi \in C_0^\infty(\mathbb{R}^{2d})$. Then by assumption (21) and the compact embedding $W^{1,\infty}([-T,T]) \hookrightarrow C([-T,T])$, $f_{\epsilon,\phi}$ converges uniformly to f_ϕ on any compact interval $[-T,T]$. In particular f_ϕ is, as a uniform limit of continuous functions, continuous, and $f_{\epsilon,\phi}(t) \to f_\phi(t)$ pointwise for all $t \in \mathbb{R}$, that is to say

$$W_\epsilon(\cdot,t) \rightharpoonup W(t) \text{ in } \mathcal{D}'(\mathbb{R}^{2d}) \text{ pointwise for all } t \in \mathbb{R}. \tag{22}$$

Now fix t. For a further subsequence which may depend on t, by Lemma 3.1 $W_{\epsilon'}(\cdot,t) \overset{*}{\rightharpoonup} \widetilde{W}(t)$ in $\mathcal{A}' \subset \mathcal{D}'$. Together with (22) this yields $W(t) = \widetilde{W}(t)$, as well as the convergence $W_\epsilon(\cdot,t) \overset{*}{\rightharpoonup} W(t)$ in $\mathcal{A}'$ for the whole sequence. By Lemma 3.1, all remaining statements about $W(t)$ follow, except its asserted continuity in t.

It remains to show the latter, i.e.

$$\int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t+h) \to \int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t) \quad (h \to 0) \quad \text{ for all } \phi \in C_0(\mathbb{R}^{2d}). \tag{23}$$

Given $\phi \in C_0(\mathbb{R}^{2d})$ and $\delta > 0$, by the density of $C_0^\infty(\mathbb{R}^{2d})$ in $C_0(\mathbb{R}^{2d})$ there exists $\phi_\delta \in C_0^\infty(\mathbb{R}^{2d})$ such that $\|\phi_\delta - \phi\|_\infty < \delta$, where $\|\cdot\|_\infty$ denotes the norm of $L^\infty(\mathbb{R}^n)$. Consequently

$$\begin{aligned}
&\Big|\int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t+h) - \int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t)\Big| \\
&\le \Big|\int_{\mathbb{R}^{2d}} \phi_\delta \,\mathrm{d}W(t+h) - \int_{\mathbb{R}^{2d}} \phi_\delta \,\mathrm{d}W(t)\Big| + \Big|\int_{\mathbb{R}^{2d}} (\phi - \phi_\delta) \,\mathrm{d}W(t+h)\Big| + \Big|\int_{\mathbb{R}^{2d}} (\phi - \phi_\delta) \,\mathrm{d}W(t)\Big| \\
&\le \Big|\int_{\mathbb{R}^{2d}} \phi_\delta \,\mathrm{d}W(t+h) - \int_{\mathbb{R}^{2d}} \phi_\delta \,\mathrm{d}W(t)\Big| + \delta\Big(\int_{\mathbb{R}^{2d}} \mathrm{d}W(t+h) + \int_{\mathbb{R}^{2d}} \mathrm{d}W(t)\Big).
\end{aligned}$$

As $h \to 0$, the first term vanishes by the continuity of $\int_{\mathbb{R}^{2d}} \phi_\delta \,\mathrm{d}W(t) = f_{\phi_\delta}(t)$ in t (which was already established above). The second term stays bounded by $2C\delta$ by Lemma 3.1, (iii), giving

$$\limsup_{h \to 0} \Big|\int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t+h) - \int_{\mathbb{R}^{2d}} \phi \,\mathrm{d}W(t)\Big| \le 2C\delta.$$

Since δ was arbitrary, the continuity assertion (23) follows, and the proof of Lemma 3.2 is complete. □

Remark Functional analytically, Lemma 3.2 says that under the assumptions (20), (21), $\{W_\epsilon\}$ is relatively compact in $C_{weak*,\ell oc}(\mathbb{R}; \mathcal{A}')$. This may be viewed as a weak-convergence variant of the well known compactness lemma of J. L. Lions [Lio69, Chap. 1, Théorème 5.1], in which the condition of boundedness of time derivatives in some Banach space has been replaced by condition (21) which is related to a weak topology.

We close this section by applying the above lemma to prove the first two statements of Theorem 1.1.

Proof of Theorem 1.1 (i) This follows from $\|\Psi_\epsilon(t)\| = \|\Psi_\epsilon^0\| = 1$, Lemma 3.2 (i), and the fact that weak* convergence in $L^\infty(\mathbb{R}; \mathcal{A}')$ implies convergence in $\mathcal{D}'(\mathbb{R}^{2d+1})$. □

Proof of Theorem 1.1 (ii) First we prove that $W \in C_{weak*}(\mathbb{R}; \mathcal{M}(\mathbb{R}^{2d}))$, $W(t) \ge 0$. By the Lemma 3.2, all we need to show is that for any function $\phi \in C_0^\infty(\mathbb{R}^{2d})$ on phase space, the expected value

$$f_{\epsilon,\phi}(t) = \int_{\mathbb{R}^{2d}} W_\epsilon(x,p,t)\phi(x,p)\,\mathrm{d}(x,p)$$

is differentiable in t and satisfies hypothesis (21) of Lemma 3.2 (ii), i.e. $f'_{\epsilon,\phi}(t)$ stays bounded independently of ϵ and t. Differentiability in t holds even for $\phi \in \mathrm{L}^1(\mathbb{R}^{2d})$, since $W_\epsilon \in \mathrm{C}^1(\mathbb{R};\mathrm{L}^\infty(\mathbb{R}^{2d}))$ by Lemma 2.1.

To deduce (21) we start by exploiting the Wigner equation (WE). This yields

$$\begin{aligned}|f'_{\epsilon,\phi}(t)| \leq & \Big| \int_{\mathbb{R}^{2d}} W_\epsilon(x,p,t)\, p\cdot\nabla_x\phi(x,p)\,\mathrm{d}(x,p)\Big| \\ &+ \Big|\frac{1}{(2\pi)^d}\int_{\mathbb{R}^{2d}} \frac{U_b(x+\frac{\epsilon y}{2})-U_b(x-\frac{\epsilon y}{2})}{\epsilon}\Psi_\epsilon(x+\frac{\epsilon y}{2},t)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}(\mathcal{F}_p\phi)(x,y)\,\mathrm{d}(x,y)\Big| \\ &+ \Big|\frac{1}{(2\pi)^d}\int_{\mathbb{R}^{2d}} \frac{U_s(x+\frac{\epsilon y}{2})-U_s(x-\frac{\epsilon y}{2})}{\epsilon}\Psi_\epsilon(x+\frac{\epsilon y}{2},t)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}(\mathcal{F}_p\phi)(x,y)\,\mathrm{d}(x,y)\Big|.\end{aligned}$$

The first term on the right hand side is bounded by $\frac{1}{(2\pi)^d}\|\Psi_\epsilon(\cdot,t)\|^2\|p\cdot\nabla_x\phi\|_{\mathcal{A}}$ by (18), and hence bounded independently of ϵ and t, by (4) and $\|\Psi^0_\epsilon\| = 1$.

Thanks to the elementary inequality $|\frac{U_b(x+\frac{\epsilon y}{2})-U_b(x-\frac{\epsilon y}{2})}{\epsilon}| \leq \|\nabla U_b\|_\infty |y|$, the second term is bounded independently of ϵ and t by

$$\frac{1}{(2\pi)^d}\|\nabla U_b\|_\infty \int_{\mathbb{R}^d} |y| \sup_{x\in\mathbb{R}} |(\mathcal{F}_p\phi)(x,y)|\,\mathrm{d}y.$$

Finally, in order to estimate the third term we observe that for $R, Q \in \mathbb{R}^n$

$$\frac{1}{\epsilon}\left|\frac{1}{|R+\frac{\epsilon Q}{2}|}-\frac{1}{|R-\frac{\epsilon Q}{2}|}\right| \leq \frac{|Q|}{|R+\frac{\epsilon Q}{2}|\,|R-\frac{\epsilon Q}{2}|}.$$

Hence, with $x = (R_1,\ldots,R_M)$, $y = (Q_1,\ldots,Q_M)$ and setting $R = R_\alpha - R_\beta$, $Q = Q_\alpha - Q_\beta \in \mathbb{R}^3$, the third term is bounded by

$$\begin{aligned}&\frac{1}{(2\pi)^d}\sum_{1\leq\alpha<\beta\leq M} C_{\alpha\beta}\|\frac{1}{|R_\alpha-R_\beta|}\Psi_\epsilon(\cdot,t)\|^2 \int_{\mathbb{R}^d} |Q_\alpha - Q_\beta| \sup_{x\in\mathbb{R}}|(\mathcal{F}_p\phi)(x,y)|\,\mathrm{d}y \\ &\leq \frac{1}{(2\pi)^d}\frac{2}{m}\|U_s\Psi_\epsilon(\cdot,t)\|^2\int_{\mathbb{R}^d}|y|\sup_{x\in\mathbb{R}}|(\mathcal{F}_p\phi)(x,y)|\,\mathrm{d}y,\end{aligned}$$

where $m = \min\{C_{\alpha\beta}\,|\,C_{\alpha\beta}\neq 0\}$. But the right hand side stays bounded independently of ϵ and t thanks to Lemma 5.1, establishing hypothesis (21) and thus completing the proof that $W \in \mathrm{C}_{weak*}(\mathbb{R};\mathcal{M}(\mathbb{R}^{2d}))$, $W(t) \geq 0$.

It remains to show that $\int_{\mathbb{R}^{2d}} \mathrm{d}W(t) = 1$ for every t. In Lemma 3.2 (ii) we proved that $W_\epsilon(\cdot,t)$ converges weak* in $\mathcal{A}'$ to $W(t)$ for every t. Hence Lemma 3.1 (iv) is applicable and it suffices to verify that both the sequence of position densities $|\Psi_\epsilon(\cdot,t)|^2$ and momentum densities $|\frac{1}{(2\pi\epsilon)^{d/2}}(\mathcal{F}\Psi_\epsilon)(\frac{p}{\epsilon},t)|^2$ are tight. As regards the momentum densities, this follows from uniform boundedness of kinetic energy, (53), since

$$\begin{aligned}\frac{1}{2}\int_{|p|\geq R}\Big|\frac{1}{(2\pi\epsilon)^{d/2}}(\mathcal{F}\Psi_\epsilon)(\tfrac{p}{\epsilon},t)\Big|^2\mathrm{d}p &\leq \frac{1}{R^2}\frac{1}{2}\int_{\mathbb{R}^d}\Big|\frac{1}{(2\pi\epsilon)^{d/2}}(\mathcal{F}\Psi_\epsilon)(\tfrac{p}{\epsilon},t)\Big|^2|p|^2\,\mathrm{d}p \\ &= \frac{1}{R^2}\frac{1}{2}\int_{\mathbb{R}^d}|\epsilon\nabla\Psi_\epsilon(x,t)|^2\,\mathrm{d}x.\end{aligned}$$

Finally, tightness of the position densities follows (under much weaker hypotheses on potential and initial data) from the Lemma 3.3 below, completing the proof of Theorem 1.1 (ii). ☐

Lemma 3.3 *(Propagation of tightness) Let U be as in* (3)*, and suppose in addition U bounded from below. Let $\{\Psi_\epsilon\}$ be a sequence of solutions to the time-dependent Schrödinger equation (SE), whose initial data satisfy $\Psi_\epsilon^0 \in \mathrm{H}^2(\mathbb{R}^d)$, $\|\Psi_\epsilon^0\| = 1$ (normalization), and $\langle \Psi_\epsilon^0, H_\epsilon \Psi_\epsilon^0 \rangle \leq C$ (bounded energy). If the sequence of initial position densities $\{|\Psi_\epsilon^0|^2\}$ is tight, then so is $\{|\Psi_\epsilon(\cdot,t)|^2\}$, for all $t \in \mathbb{R}$.*

Proof of Lemma 3.3 Let $\chi \in \mathrm{C}_0^\infty(\mathbb{R}^d)$, $0 \leq \chi \leq 1$, $\chi = 1$ on $|x| > 1$, $\chi = 0$ on $|x| < 1/2$, and for $R > 0$ set $\chi_R(x) := \chi(x/R)$. Then $|\nabla \chi_R| \leq C/R$, $|\Delta \chi_R| \leq C/R^2$ for some constant C independent of R. Letting $\langle \cdot, \cdot \rangle$ be the $\mathrm{L}^2(\mathbb{R}^d)$ inner product and abbreviating $\langle A \rangle_\phi = \langle \phi, A\phi \rangle$, we obtain from (SE)

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \chi_R \rangle_{\Psi_\epsilon(\cdot,t)} = \frac{i}{\epsilon} \langle [\chi_R, H_\epsilon] \rangle_{\Psi_\epsilon(\cdot,t)}.$$

Since $[\chi_R, H_\epsilon] = \frac{\epsilon^2}{2} \Delta \chi_R + \epsilon^2 \nabla \chi_R \cdot \nabla$,

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \langle \chi_R \rangle_{\Psi_\epsilon(\cdot,t)} &\leq \frac{\epsilon}{2} \int_{\mathbb{R}^d} |\Delta \chi_R(x)|\, |\Psi_\epsilon(x,t)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^d} |\epsilon \nabla \Psi_\epsilon(x,t)|\, |\nabla \chi_R(x)|\, |\Psi_\epsilon(x,t)| \,\mathrm{d}x \\ &\leq \frac{\epsilon}{2} \|\Delta \chi_R\|_\infty \|\Psi_\epsilon(\cdot,t)\| + \|\nabla \chi_R\|_\infty \|\epsilon \nabla \Psi_\epsilon(\cdot,t)\| \, \|\Psi_\epsilon(\cdot,t)\|. \end{aligned}$$

¿From the boundedness from below of U and the conservation in time of the energy $\langle \Psi_\epsilon(\cdot,t), H_\epsilon \Psi_\epsilon(\cdot,t) \rangle$, we obtain $\|\epsilon \nabla \Psi_\epsilon(\cdot,t)\| \leq$ *const.* for some constant independent of ϵ and t. Using the bounds on $\|\nabla \chi_R\|_\infty$ and $\|\Delta \chi_R\|_\infty$, and assuming without loss of generality $\epsilon \leq R$, it follows that $\frac{\mathrm{d}}{\mathrm{d}t} \langle \chi_R \rangle_{\Psi_\epsilon(\cdot,t)} \leq \frac{const.}{R}$ for some constant independent of ϵ and t. Consequently (considering without loss of generality $t \geq 0$)

$$\int_{|x|>R} |\Psi_\epsilon(x,t)|^2 \,\mathrm{d}x \leq \langle \chi_R \rangle_{\Psi_\epsilon(\cdot,t)} \leq \langle \chi_R \rangle_{\Psi_\epsilon^0} + \int_{s=0}^t \frac{const.}{R} \,\mathrm{d}s \leq \int_{|x|>\frac{R}{2}} |\Psi_\epsilon^0(x)|^2 \,\mathrm{d}x + \frac{const.}{R} t \to 0$$

as $R \to \infty$, by the tightness of the sequence of initial position densitites. □

4 Justification of the Liouville equation

We now show that time-dependent Wigner measures arising as a limit of semiclassically scaled solutions to the Schrödinger equation are weak solutions of the Liouville equation (LE).

In line with the discussion in the Introduction, the main work will go into analyzing the behaviour near the Coulomb singularities. The first order of business will be to verify that the limit equation even makes sense, for which we need that the gradient of the potential lies in L^1 with respect to the Wigner measure, for all t.

We note the particularly impeding feature that the singularities of the Coulomb forces appearing in the Liouville equation have the magnitude $1/|R_\alpha - R_\beta|^2$, and are hence much worse than the singularities of the Coulomb potentials $1/|R_\alpha - R_\beta|$ appearing in the original Schrödinger equation.

Proof of Theorem 1.1 (iii) We want to show that

$$W(t)(\mathcal{S} \times \mathbb{R}^d) = 0, \tag{24}$$

$$\int_{\mathbb{R}^{2d}} |\nabla U_s| \,\mathrm{d}W(t) < \infty \quad \text{for all } t \in \mathbb{R}. \tag{25}$$

To this end, we fix $t \in \mathbb{R}$ and choose a subsequence such that $|\Psi_\epsilon(\cdot,t)|^2 \overset{*}{\rightharpoonup} \mu$ in $\mathcal{M}(\mathbb{R}^d)$. According to Lemma 3.1 (iii) we have

$$\int_{p\in\mathbb{R}^d} W(\cdot,\mathrm{d}p,t) \le \mu. \tag{26}$$

First we show $W(t)(\mathcal{S}\times\mathbb{R}^d)=0$. By (26) it suffices to show that $\mu(\mathcal{S})=0$. Let $\phi\in \mathrm{C}(\mathbb{R}^d)$ with $0\le\phi\le 1$, $\phi=1$ for $\mathrm{dist}(x,\mathcal{S})<\delta$, and $\phi=0$ for $\mathrm{dist}(x,\mathcal{S})\ge 2\delta$. We use the elementary property of weak* convergence in $\mathcal{M}(\mathbb{R}^d)$ that if $\mu_\epsilon\ge 0$, $\mu_\epsilon \overset{*}{\rightharpoonup} \mu$ in $\mathcal{M}(\mathbb{R}^d)$, and f is a bounded nonnegative continuous function, then $\int_{\mathbb{R}^d} f\,\mathrm{d}\mu \le \liminf_{\epsilon\to 0}\int_{\mathbb{R}^d} f\,\mathrm{d}\mu_\epsilon$. (This follows immediately by approximating f by compactly supported functions f_j with $0\le f_j\le f$ and dominated convergence.) Consequently

$$\int_{\mathrm{dist}(x,\mathcal{S})\le\delta}\mathrm{d}\mu \le \int_{\mathbb{R}^d}\phi\,\mathrm{d}\mu \le \liminf_{\epsilon\to 0}\int_{\mathbb{R}^d}\phi\,|\Psi_\epsilon(\cdot,t)|^2\,\mathrm{d}x = \liminf_{\epsilon\to 0}\int_{\mathrm{dist}(x,\mathcal{S})\le 2\delta}|\Psi_\epsilon(\cdot,t)|^2\,\mathrm{d}x.$$

The idea now is to use the fact that $U_s\ge\frac{1}{\widetilde{C}\delta}$ on $\{x\in\mathbb{R}^d\,|\,\mathrm{dist}(x,\mathcal{S})\le 2\delta\}$ for some constant $\widetilde{C}$, and appeal to Lemma 5.1 below. This yields

$$\int_{\mathrm{dist}(x,\mathcal{S})\le\delta}\mathrm{d}\mu \le \Big(\widetilde{C}\delta\Big)^2\liminf_{\epsilon\to 0}\int_{\mathbb{R}^d}U_s^2|\Psi_\epsilon(\cdot,t)|^2\,\mathrm{d}x \le \Big(\widetilde{C}\delta\Big)^2 C. \tag{27}$$

Since the RHS tends to zero as $\delta\to 0$, $\mu(\mathcal{S})=0$ and $W(t)(\mathcal{S}\times\mathbb{R}^d)=0$, completing the proof of (24).

To show (25) we will use the monotone convergence theorem. To this end we set for $\delta>0$

$$f_\delta := \min\Big\{f,\frac{1}{\delta}\Big\},\quad f:=|\nabla U_s|.$$

Then f_δ is a bounded continuous function on $\mathbb{R}^d$. By the fact that $|\nabla U_s|\le C_0U_s^2$ (thanks to the identity $\left|\nabla_{R_\alpha}\frac{1}{|R_\alpha-R_\beta|}\right| = \frac{1}{|R_\alpha-R_\beta|^2}$) and Lemma 5.1 below,

$$\int_{\mathbb{R}^d} f_\delta\,\mathrm{d}\mu \le \liminf_{\epsilon\to 0}\int_{\mathbb{R}^d} f_\delta|\Psi_\epsilon(\cdot,t)|^2\,\mathrm{d}x \le C_0\liminf_{\epsilon\to 0}\int_{\mathbb{R}^d}U_s^2|\Psi_\epsilon(\cdot,t)|^2\,\mathrm{d}x \le C_0C, \tag{28}$$

where C_0, C are constants independent of ϵ and t.

Consider now the limit $\delta\to 0$. In this limit, $f_\delta\to f$ monotonically on $\mathbb{R}^d\backslash\mathcal{S}$. Since $\mu(\mathcal{S})=0$, it follows that $f_\delta\to f$ μ-almost everywhere. Hence the monotone convergence theorem yields $f\in \mathrm{L}^1(\mathrm{d}\mu)$ and

$$\int_{\mathbb{R}^d} f\,\mathrm{d}\mu = \lim_{\delta\to 0}\int_{\mathbb{R}^d} f_\delta\,\mathrm{d}\mu. \tag{29}$$

Consequently, by the p-independence of f, (26), (29), (28),

$$\int_{\mathbb{R}^{2d}} f\,\mathrm{d}W(t) \le \int_{\mathbb{R}^d} f\,\mathrm{d}\mu \le C_0C<\infty, \tag{30}$$

establishing (25) and completing the proof of (iii). □

Proof of Theorem 1.1 (iv) Let $\Omega\subseteq\mathbb{R}^d$ be an open set such that $U_b\in \mathrm{C}^1(\Omega)$. We need to show that eq. (8) holds for every $\phi\in \mathrm{C}_0^\infty(\Omega\times\mathbb{R}^d\times\mathbb{R})$. Starting point is the fact that by Lemma

2.1, W_ϵ satisfies the Wigner equation (WE). Multiplying (WE) by ϕ and integrating by parts, we obtain the weak form

$$\int_{\mathbb{R}^{2d+1}} \Big(W_\epsilon(\partial_t + p\cdot\nabla_x)\phi + f_\epsilon\phi \Big)\,\mathrm{d}(x,p,t) = 0. \tag{31}$$

Passage to the limit $\epsilon \to 0$ in eq. (31) is done in three steps, carried out in the order of increasing difficulty: 1. Analysis of the local terms, 2. Analysis of the nonlocal term $\int f_\epsilon\phi$ for test functions vanishing in a neighbourhood of the Coulomb singularities, 3. Analysis of the nonlocal term in a neighbourhood of the Coulomb singularities.

Step 1: Analysis of the local terms in (31)

As $\epsilon \to 0$, $W_\epsilon \overset{*}{\rightharpoonup} W$ in $\mathrm{L}^\infty(\mathbb{R};\mathcal{A}')$, and hence in particular in $\mathcal{D}'(\mathbb{R}^{2d+1})$. Thus, the first term in (31) satisfies

$$\int_{\mathbb{R}^{2d+1}} W_\epsilon\,(\partial_t + p\cdot\nabla_x)\phi\,\mathrm{d}(x,p,t) \to \int_{\mathbb{R}}\int_{\mathbb{R}^{2d}} (\partial_t + p\cdot\nabla_x)\phi\,\mathrm{d}W(t)\,\mathrm{d}t \quad (\epsilon\to 0). \tag{32}$$

Step 2: Analysis of the nonlocal term $\int f_\epsilon\phi$ for test functions vanishing in a neighbourhood of the Coulomb singularities

Let $\mathcal{S}\subset\mathbb{R}^d$ be the set of Coulomb singularities of the potential U_s (see Theorem 1.1 (iii)). Our goal in this step is to prove that

$$\int_{\mathbb{R}^{2d+1}} f_\epsilon\,\phi\,\mathrm{d}(x,p,t) \to -\int_{\mathbb{R}}\int_{\mathbb{R}^{2d}} \nabla U\cdot\nabla_p\phi\,\mathrm{d}W(t)\,\mathrm{d}t \quad (\epsilon\to 0) \tag{33}$$

for all test functions on $\Omega\times\mathbb{R}^d\times\mathbb{R}$ which vanish in a neighbourhood of $\mathcal{S}$, i.e., $\phi\in \mathrm{C}_0^\infty((\Omega\backslash\mathcal{S})\times\mathbb{R}^d\times\mathbb{R})$. This together with (31), (32) completes the proof of (iv) for the above test functions.

We begin by rewriting the left hand side of (33). Substituting the definition of f_ϵ and carrying out the integration over p gives (abbreviating $\Psi_\epsilon = \Psi_\epsilon(x+\frac{\epsilon y}{2},t)$, $\overline{\Psi_\epsilon} = \overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)}$, $\mathcal{F}_p\phi = (\mathcal{F}_p\phi)(x,y,t)$)

$$\int_{\mathbb{R}^{2d+1}} f_\epsilon\,\phi\,\mathrm{d}(x,p,t) = -\frac{i}{(2\pi)^d}\int_{\mathbb{R}^{2d+1}} \frac{U(x+\frac{\epsilon y}{2}) - U(x-\frac{\epsilon y}{2})}{\epsilon}\Psi_\epsilon\overline{\Psi_\epsilon}(\mathcal{F}_p\phi)\,\mathrm{d}(x,y,t). \tag{34}$$

The idea now is to split the y-integration into two regions in such a way that either $|\epsilon y| << 1$, in which case the difference quotient of U is well approximated by the derivative $\nabla U(x)\cdot y$, or $|y| >> 1$, in which case $\mathcal{F}_p\phi$ is very small, due to the rapid decay of the Schwartz function $\mathcal{F}_p\phi$ as $|y|\to\infty$. To implement this idea, we introduce a cut off radius $\epsilon^{-\alpha}$ with some fixed $\alpha\in(0,1)$ and choose the regions of integration as $|y|\le\epsilon^{-\alpha}$ and $|y|>\epsilon^{-\alpha}$. In particular, we denote $\Lambda^\epsilon := \{(y,t)\in\mathbb{R}^{d+1}\,|\,|y|\le\epsilon^{-\alpha}\}$ and $V_\epsilon := \{(y,t)\in\mathbb{R}^{d+1}\,|\,|y|>\epsilon^{-\alpha}\}$. It is also convenient to subtract off, and then add again, the RHS of (34) with the difference quotient of U replaced by the derivative $\nabla U(x)\cdot y$. This yields the following natural splitting of the RHS of (34) into a sum of five terms

$$\int_{\mathbb{R}^{2d+1}} f_\epsilon\,\phi\,\mathrm{d}(x,p,t) = \; T_1 + T_2^+ + T_2^- + T_3 + T_4, \tag{35}$$

$$T_1 := -\frac{i}{(2\pi)^d}\int_{\mathbb{R}^d\times\Lambda^\epsilon}\Big[\frac{U(x+\frac{\epsilon y}{2})-U(x-\frac{\epsilon y}{2})}{\epsilon} - \nabla U(x)\cdot y\Big]\frac{1}{|y|}\cdot|y|\,\Psi_\epsilon\overline{\Psi_\epsilon}(\mathcal{F}_p\phi)\,\mathrm{d}(x,y,t),$$

$$T_2^\pm := \mp\frac{i}{(2\pi)^d}\int_{\mathbb{R}^d\times V_\epsilon}\frac{U(x\pm\frac{\epsilon y}{2})}{\epsilon}\,\Psi_\epsilon\overline{\Psi_\epsilon}(\mathcal{F}_p\phi)\,\mathrm{d}(x,y,t),$$

$$T_3 := \frac{i}{(2\pi)^d}\int_{\mathbb{R}^d\times V_\epsilon}\nabla U(x)\cdot y\,\Psi_\epsilon\overline{\Psi_\epsilon}(\mathcal{F}_p\phi)\,\mathrm{d}(x,y,t),$$

$$T_4 := -\frac{i}{(2\pi)^d}\int_{\mathbb{R}^{2d+1}}\nabla U(x)\cdot y\,\Psi_\epsilon\overline{\Psi_\epsilon}(\mathcal{F}_p\phi)\,\mathrm{d}(x,y,t).$$

Here, in T_1 the factor $\frac{1}{|y|}\cdot|y| = 1$ has been inserted for future use.

We begin by analysing T_1. Let $\delta,\,R > 0$ such that the set $\Omega_{R,\delta} := \{x\in\Omega\,|\,|x|\le R,\,\mathrm{dist}(x,\mathcal{S}\cup\partial\Omega)\ge\delta\}$ contains all x with $(x,p,t)\in\operatorname{supp}\phi$. Then provided ϵ is sufficiently small

$$|x\pm\frac{\epsilon y}{2}|\le 2R,\;\;\mathrm{dist}(x\pm\frac{\epsilon y}{2},\mathcal{S}\cup\partial\Omega)\ge\frac{\delta}{2}\qquad\text{for all } x\in\Omega_{R,\delta},\;|y|\le\epsilon^{-\alpha},$$

that is to say $x\pm\frac{\epsilon y}{2}\in\Omega_{2R,\delta/2}$. Hence by the continuous differentiability of U in $\Omega_{2R,\delta/2}$,

$$\frac{U(x+\frac{\epsilon y}{2})-U(x-\frac{\epsilon y}{2})}{\epsilon|y|}\to\nabla U(x)\cdot\frac{y}{|y|}\qquad\text{as }\epsilon\to 0\text{ uniformly for } x\in\Omega_{R,\delta},\;|y|\le\epsilon^{-\alpha}.$$

Consequently, applying the Cauchy-Schwarz inequality with respect to the integration over x, T_1 can be estimated by

$$|T_1|\le\frac{1}{(2\pi)^d}\sup_{x\in\Omega_{R,\delta},\,|y|\le\epsilon^{-\alpha}}\left|\frac{U(x+\frac{\epsilon y}{2})-U(x-\frac{\epsilon y}{2})}{\epsilon|y|}-\nabla U(x)\cdot\frac{y}{|y|}\right|\sup_{t\in\mathbb{R}}\|\Psi_\epsilon(\cdot,t)\|^2\,\|y\mathcal{F}_p\phi\|_*\to 0 \tag{36}$$

as $\epsilon\to 0$, where here and below, for any function $\chi\in\mathcal{S}(\mathbb{R}^{2d+1})$ we denote

$$\|\chi\|_* := \int_{\mathbb{R}^{d+1}}\sup_{x\in\mathbb{R}^d}|\chi(x,y,t)|\,\mathrm{d}(y,t). \tag{37}$$

The terms $T_2^\pm$ can be estimated in an analogous manner, again applying the Cauchy-Schwarz inequality with respect to the integration over x:

$$|T_2^\pm|\le\frac{1}{(2\pi)^d}\sup_{t\in\mathbb{R}}\|U\Psi_\epsilon(\cdot,t)\|\,\sup_{t\in\mathbb{R}}\|\Psi_\epsilon(\cdot,t)\|\,\frac{1}{\epsilon}\int_{V_\epsilon}\sup_{x\in\mathbb{R}^d}|(\mathcal{F}_p\phi)(x,y,t)|\,\mathrm{d}(y,t). \tag{38}$$

By Lemma 5.1 and the boundedness of U_b, the norm $\|U\Psi_\epsilon(\cdot,t)\|$ stays bounded independently of t and ϵ. On the other hand, since $\mathcal{F}\phi\in\mathcal{S}(\mathbb{R}^{2d+1})$,

$$\sup_{(x,y,t)\in\mathbb{R}^{2d+1}}(1{+}|y|)^m|(\mathcal{F}_p\phi)(x,y,t)| =: c_m < \infty$$

for any $m = 0,1,2,\ldots$. Consequently, for all $m\ge d+1$ and all $|y|>\epsilon^{-\alpha}$

$$|(\mathcal{F}_p\phi)(x,y,t)|\le\frac{c_m}{(1{+}|y|)^m}\le\frac{c_m}{(1{+}|y|)^{d+1}}\frac{1}{(\epsilon^{-\alpha})^{m-d-1}} = \frac{c_m}{(1{+}|y|)^{d+1}}\epsilon^{\alpha(m-d-1)}.$$

Hence, choosing T so large that $|t| \le T$ for all $(x,p,t) \in \operatorname{supp}\phi$, the last factor in (38) satisfies

$$\int_{V_\epsilon} \sup_{x\in\mathbb{R}^d} |(\mathcal{F}_p\phi)(x,y,t)| \,\mathrm{d}(y,t) \le \epsilon^{\alpha(m-d-1)} \int_{\mathbb{R}^d} \frac{2Tc_m}{(1+|y|)^{d+1}} \,\mathrm{d}y. \tag{39}$$

Then, if m is chosen so large that the exponent $\alpha(m-d-1) > 1$, the positive power of ϵ in (39) 'beats' the singular factor $\frac{1}{\epsilon}$ in (38). Thus

$$T_2^{\pm} \to 0 \text{ as } \epsilon \to 0 \tag{40}$$

(in fact, faster than any power of ϵ, but this is not needed in the sequel).

The proof that $T_3 \to 0$ is analogous but easier, due to the absence of a singular prefactor $\frac{1}{\epsilon}$ and the fact that $\nabla U(x)$, unlike $U(x \pm \epsilon y/2)$, is bounded on $\operatorname{supp}\phi$. We simply estimate

$$|T_3| \le \frac{1}{(2\pi)^d} \sup_{x\in\Omega_{R,\delta}} |\nabla U(x)| \int_{V_\epsilon} |y| \sup_{x\in\mathbb{R}^d} |(\mathcal{F}_p\phi)(x,y,t)| \,\mathrm{d}(y,t) \to 0 \text{ as } \epsilon \to 0 \tag{41}$$

by (39) with $m > d+2$.

Finally, consider the last term, T_4. Using $iy\mathcal{F}_p\phi = \mathcal{F}_p(\nabla_p\phi)$ and interchanging the integrations over p and y,

$$\begin{aligned} T_4 &= -\frac{1}{(2\pi)^d} \int_{\mathbb{R}^{2d+1}} \nabla U(x) \cdot \Big[\int_{\mathbb{R}^d} \nabla_p\phi(x,p,t) e^{-ip\cdot y} \,\mathrm{d}p\Big] \Psi_\epsilon(x+\frac{\epsilon y}{2},t)\overline{\Psi_\epsilon(x-\frac{\epsilon y}{2},t)} \,\mathrm{d}(x,y,t) \\ &= -\int_{\mathbb{R}^{2d+1}} \nabla U(x) \cdot \nabla_p\phi(x,p,t)\, W_\epsilon(x,p,t) \,\mathrm{d}(x,p,t). \end{aligned}$$

Since $\nabla U \cdot \nabla_p\phi \in \mathrm{L}^1(\mathbb{R};\mathcal{A})$ due to the continuity of ∇U on $\operatorname{supp}\phi$, and since $W_\epsilon \overset{*}{\rightharpoonup} W$ in the dual $\mathrm{L}^\infty(\mathbb{R};\mathcal{A}')$,

$$T_4 \to -\int_{\mathbb{R}} \int_{\mathbb{R}^{2d}} \nabla U(x) \cdot \nabla_p\phi(x,p,t) \,\mathrm{d}W(t) \,\mathrm{d}t \text{ as } \epsilon \to 0. \tag{42}$$

Combining (36), (40), (41), (42) yields (33) for $\phi \in \mathrm{C}_0^\infty((\Omega \setminus \mathcal{S}) \times \mathbb{R}^d \times \mathbb{R})$.

Step 3: Analysis of the nonlocal term $\int f_\epsilon\phi$ in a neighbourhood of the Coulomb singularities

We prove here that eq. (33) continues to hold for arbitrary $\phi \in \mathrm{C}_0^\infty(\Omega \times \mathbb{R}^d \times \mathbb{R})$ not required to vanish in a neighbourhood of the Coulomb singularities, i.e. that the Liouville equation continues to hold across Coulomb singularities.

This is quite remarkable, since the available a priori bound $\int_{\mathbb{R}^d} U_s^2 |\Psi_\epsilon(\cdot,t)|^2 \le \mathit{const.}$ only rules out concentration of the measure $|\Psi_\epsilon(\cdot,t)|^2$ on Coulomb singularities (as was shown in (27)), but not concentration of the blown-up measure $U_s^2|\Psi_\epsilon(\cdot,t)|^2 \sim |\nabla U_s|\,|\Psi_\epsilon(\cdot,t)|^2$ which asymptotically appears in $\int f_\epsilon\phi$ (see the leading term T_4 in (35)). This suggests the possibility that an additional contribution of form $\int_{\mathbb{R}} \int_{\mathcal{S}\times\mathbb{R}^d} \phi \,\mathrm{d}\nu(t)\,\mathrm{d}t$, with $\nu(t)$ a singular measure supported on $\mathcal{S} \times \mathbb{R}^d$, could appear in the limit equation (8).

This possibility will be ruled out by careful use of the evolution equation (WE) satisfied by W_ϵ. Roughly, our analysis below will lead to the insight that the asymptotic amount of mass of f_ϵ in a δ-neighbourhood of the singular set $\mathcal{S}$ is at most of order δ, not order one.

We will need rather precisely chosen cutoff functions. Given $\delta > 0$, we let

$$\eta_\delta(x) := \prod_{1\le\alpha<\beta\le M} \eta\Big(\frac{|R_\alpha - R_\beta|}{\delta}\Big) \quad \text{with } x = (R_1, \ldots, R_m),$$

where $\eta \in \mathrm{C}_0^\infty(\mathbb{R})$ with $0 \le \eta \le 1$, $\eta = 1$ on $|z| \le 1/2$, $\eta = 0$ on $|z| \ge 1$. Then for some constants C_1, C_2 independent of δ

$$|\nabla \eta_\delta(x)| \le \frac{C_1}{\delta} \text{ for all } x, \quad \eta_\delta(x) = 0 \text{ for } \mathrm{dist}(x, \mathcal{S}) \ge C_2\delta. \tag{43}$$

We now write $\phi = (1-\eta_\delta)\phi + \eta_\delta\phi$, and consider both contributions to $\int_{\mathbb{R}^{2d+1}} f_\epsilon \phi \, \mathrm{d}(x,p,t)$ separately. Since $(1-\eta_\delta)\phi$ belongs to $\mathrm{C}_0^\infty((\Omega \setminus \mathcal{S}) \times \mathbb{R}^d \times \mathbb{R})$, we have by Step 2 (cf. (33))

$$\int_{\mathbb{R}^{2d+1}} f_\epsilon \,(1-\eta_\delta)\phi \, \mathrm{d}(x,p,t) \to -\int_{\mathbb{R}} \int_{\mathbb{R}^{2d}} \nabla U \cdot (1-\eta_\delta)\nabla_p \phi \, \mathrm{d}W(t) \, \mathrm{d}t \quad \text{as } \epsilon \to 0. \tag{44}$$

We now claim that the remaining terms are small when δ is small, that is to say

$$\limsup_{\epsilon \to 0} \Big| \int_{\mathbb{R}^{2d+1}} f_\epsilon \, \eta_\delta \phi \, \mathrm{d}(x,p,t) \Big| \to 0 \text{ as } \delta \to 0, \tag{45}$$

$$\int_{\mathbb{R}} \int_{\mathbb{R}^{2d}} \nabla U \cdot \eta_\delta \nabla_p \phi \, \mathrm{d}W(t) \, \mathrm{d}t \to 0 \text{ as } \delta \to 0. \tag{46}$$

Clearly, (44) and (45), (46) imply eq. (33) for the arbitrary test function $\phi \in \mathrm{C}_0^\infty(\Omega \times \mathbb{R}^d \times \mathbb{R})$.

Proving (46) is not difficult, but for convenience of the reader we include a proof. Consider first a fixed t. By the facts that $0 \le \eta_\delta \le 1$ and $\mathrm{supp}\, \eta_\delta \subset \{x \in \mathbb{R}^d \,|\, \mathrm{dist}(x, \mathcal{S}) \le C_2\delta\}$,

$$\Big| \int_{\mathbb{R}^{2d}} \nabla U \cdot \eta_\delta \nabla_p \phi \, \mathrm{d}W(t) \Big| \le \|\nabla_p \phi\|_\infty \int_{(\mathrm{supp}\, \eta_\delta \cap \mathrm{supp}\, \phi) \times \mathbb{R}^d} |\nabla U| \, \mathrm{d}W(t) \tag{47}$$

$$\to \|\nabla_p \phi\|_\infty \int_{(\mathcal{S} \cap \mathrm{supp}\, \phi) \times \mathbb{R}^d} |\nabla U| \, \mathrm{d}W(t) = 0 \text{ as } \delta \to 0,$$

since $\mathrm{d}W(t)(\mathcal{S} \times \mathbb{R}^d) = 0$ and $\nabla U \in \mathrm{L}^1(\mathrm{supp}\, \phi; \mathrm{d}W(t))$. Moreover the LHS of (47) stays bounded independently of t by (30). Hence the integrand with respect to t in (46) tends to zero boundedly a.e. as $\delta \to 0$, and so by dominated convergence we infer (46).

It remains to establish (45). This is the difficult part of Step 3, due to the fact discussed above that the a priori bound of Lemma 5.1 does not rule out the possibility of concentration of mass of $|\nabla U| |\Psi_\epsilon(\cdot, t)|^2$ on the set $\mathcal{S}$ of Coulomb singularities. Using first (WE) and then the definition of W_ϵ we have

$$\begin{aligned} &\int_{\mathbb{R}^{2d+1}} f_\epsilon \, \eta_\delta \phi \, \mathrm{d}(x,p,t) = -\int_{\mathbb{R}^{2d+1}} W_\epsilon \, (\partial_t + p \cdot \nabla_x)(\eta_\delta \phi) \, \mathrm{d}(x,p,t) \\ &= -\int_{\mathbb{R}^{2d+1}} W_\epsilon \Big[\eta_\delta (\partial_t + p \cdot \nabla_x)\phi + \nabla \eta_\delta \cdot p\phi \Big] \, \mathrm{d}(x,p,t) = -\frac{1}{(2\pi)^d} \int_{\mathbb{R}^{2d+1}} u_{\epsilon,\delta} \, \mathrm{d}(x,y,t) \\ &= \underbrace{-\frac{1}{(2\pi)^d} \int_{\mathbb{R}^d \times \Lambda^\epsilon} u_{\epsilon,\delta} \, \mathrm{d}(x,y,t)}_{=:Q_1} \underbrace{-\frac{1}{(2\pi)^d} \int_{\mathbb{R}^d \times V_\epsilon} u_{\epsilon,\delta} \, \mathrm{d}(x,y,t)}_{=:Q_2}, \end{aligned}$$

where we have split the domain of integration as in Step 2, and where

$$u_{\epsilon,\delta}(x,y,t) = \Big[\eta_\delta(x) \underbrace{\mathcal{F}_p((\partial_t + p \cdot \nabla_x)\phi)}_{=:\chi}(x,y,t) + \nabla \eta_\delta(x) \cdot \underbrace{\mathcal{F}_p(p\phi)}_{=:\xi}(x,y,t) \Big] \Psi_\epsilon(x + \frac{\epsilon y}{2}, t) \overline{\Psi_\epsilon(x - \frac{\epsilon y}{2}, t)}.$$

The second term, Q_2, is exactly of the same form as the term T_3 in Step 2, with $\nabla U(x)$ replaced by $\eta_\delta(x)$ respectively $\nabla\eta_\delta(x)$, and the test function $y\mathcal{F}_p\phi$ replaced by χ respectively ξ. Consequently, estimating as for (41),

$$|Q_2| \le \frac{1}{(2\pi)^d}\Big[\|\eta_\delta\|_\infty \int_{V_\epsilon} \sup_{x\in\mathbb{R}^d} |\chi(x,y,t)|\,\mathrm{d}(y,t) + \|\nabla\eta_\delta\|_\infty \int_{V_\epsilon} \sup_{x\in\mathbb{R}^d} |\xi(x,y,t)|\,\mathrm{d}(y,t)\Big] \to 0\ (\epsilon\to 0), \tag{48}$$

by (39) with χ respectively ξ in place of $\mathcal{F}_p\phi$, and $m > d+1$. The first term, Q_1, will be dealt with by an argument similar to the no-concentration estimate (27) in the proof of (iii), except now a non-local version is needed since the term under investigation is not local in W_ϵ. For ϵ sufficiently small, and (x,y) belonging to the domain of integration, that is to say $x \in \operatorname{supp}\eta_\delta$, $|y| \le \epsilon^{-\alpha}$, we have (writing $x = (R_1, .., R_M)$, $y = (Q_1, .., Q_M)$)

$$|(R_\alpha \pm \frac{\epsilon Q_\alpha}{2}) - (R_\beta \pm \frac{\epsilon Q_\beta}{2})| \le 2\delta \quad \text{for } 1 \le \alpha < \beta \le M$$

and consequently $U_s(x \pm \frac{\epsilon y}{2}) \ge \frac{1}{\widetilde{C}\delta}$ for $x \in \operatorname{supp}\eta_\delta$, $|y| \le \epsilon^{-\alpha}$, and some constant $\widetilde{C}$. Hence

$$\begin{aligned}|Q_1| &\le \frac{(\widetilde{C}\delta)^2}{(2\pi)^d}\int_{\mathbb{R}^d\times\Lambda^\epsilon}\Big[\eta_\delta|\chi| + |\nabla\eta_\delta|\,|\xi|\Big]\,|U_s(x+\frac{\epsilon y}{2})\Psi_\epsilon(x+\frac{\epsilon y}{2},t)|\,|U_s(x-\frac{\epsilon y}{2})\Psi_\epsilon(x-\frac{\epsilon y}{2},t)|\,\mathrm{d}(x,y,t)\\ &\le \frac{(\widetilde{C}\delta)^2}{(2\pi)^d}\Big[\|\eta_\delta\|_\infty\|\chi\|_* + \|\nabla\eta_\delta\|_\infty\|\xi\|_*\Big]\,\sup_{t\in\mathbb{R}}\|U_s\Psi_\epsilon(\cdot,t)\|^2\end{aligned}$$

with $\|\cdot\|_*$ given by (37). Since $\|U_s\Psi_\epsilon(\cdot,t)\|$ stays bounded independently of t and ϵ by Lemma 5.1, $\|\eta_\delta\|_\infty = 1$, and $\|\nabla\eta_\delta\|_\infty \le \frac{C_1}{\delta}$ by (43), it follows that

$$|Q_1| \le C_*[\delta^2 + \delta] \tag{49}$$

for some constant C_* independent of ϵ and δ. Note how the positive power of δ gained by inserting the multiplier U_s has 'beaten' the negative power of δ coming from the gradient of the cutoff function η_δ. Combining (48), (49) gives (45). This completes the proof of Theorem 1.1 (iv) for general test functions. □

5 An a priori estimate for the Schrödinger equation with repulsive Coulomb interactions

We prove now the a priori estimate used in the derivation of the Liouville equation that the potential term $U_s\Psi_\epsilon(\cdot,t)$ in the semiclassically scaled Schrödinger equation (SE) stays bounded in $\mathrm{L}^2(\mathbb{R}^d)$ independently of ϵ and t.

For potentials with Coulomb singularities, such as (2), such an estimate says in particular that in the limit $\epsilon \to 0$, the wavefunction cannot concentrate mass at the singularities.

On physical grounds, one would expect this to be true only for repulsive interactions (as present here), but not for attractive interactions. The challenge then is to translate this physical intuition into a mathematical argument fine enough to detect sign information. This is achieved by the positive commutator argument below, which exploits not just the repulsivity (i.e., positivity) of U_s, but also its special Coulombic nature.

Lemma 5.1 *Let $U = U_b + U_s$ be as in Theorem 1.1. Let $\{\Psi_\epsilon^0\} \subset \mathcal{D}(H_\epsilon)$ satisfy $\|\Psi_\epsilon^0\| = 1$ and $\|H_\epsilon \Psi_\epsilon^0\| \le c$ for some constant c independent of ϵ. Then the solution $\Psi_\epsilon(\cdot, t)$ to* (SE) *satisfies*

$$\sup_{t\in\mathbb{R}} \|U_s \Psi_\epsilon(\cdot,t)\|^2 \le C \tag{50}$$

for some constant C independent of ϵ.

Proof By standard results on the unitary propagator e^{-itH} associated to a self-adjoint operator H, if $\psi_0 \in \mathcal{D}(H)$, then so is $\psi(\cdot,t) = e^{-itH}\psi_0$ for all $t \in \mathbb{R}$, and $\|\psi(\cdot,t)\|$, $\langle \psi(\cdot,t), H\psi(\cdot,t)\rangle$, $\|H\psi(\cdot,t)\|$ are time-independent. (Formally, the time-independence follows from the Heisenberg evolution equation for expected values, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(\cdot,t), A\psi(\cdot,t)\rangle = \langle \psi(\cdot,t), \frac{1}{i}[A,H]\psi(\cdot,t)\rangle$, by taking $A = I$, H, H^2.) Applied to our case this yields, besides (4),

$$\sup_{t\in\mathbb{R}} \Big(\frac{1}{2}\int_{\mathbb{R}^d} |\epsilon\nabla\Psi_\epsilon(x,t)|^2\,\mathrm{d}x + \int_{\mathbb{R}^d} (U_b(x) + U_s(x))|\Psi_\epsilon(x,t)|^2\,\mathrm{d}x\Big) \le const., \tag{51}$$

$$\sup_{t\in\mathbb{R}} \Big\| \Big(-\frac{\epsilon^2}{2}\Delta + U_b + U_s\Big)\Psi_\epsilon(\cdot,t)\Big\|^2 \le const., \tag{52}$$

the constants being independent of ϵ. By (4), the boundedness of U_b, and the nonnegativity of U_s,

$$\sup_{t\in\mathbb{R}} \frac{1}{2}\int_{\mathbb{R}^d} |\epsilon\nabla\Psi_\epsilon(x,t)|^2\,\mathrm{d}x \le const., \qquad \sup_{t\in\mathbb{R}} \int_{\mathbb{R}^d} U_s(x)|\Psi_\epsilon(x,t)|^2\,\mathrm{d}x \le const., \tag{53}$$

all constants being independent of ϵ. Now we expand the left hand side of (52), and rewrite the latter in the form

$$\sup_{t\in\mathbb{R}} \Big(\Big\| \Big(-\frac{\epsilon^2}{2}\Delta + U_b\Big)\Psi_\epsilon(\cdot,t)\Big\|^2 + 2\mathrm{Re}\Big\langle -\frac{\epsilon^2}{2}\Delta\Psi_\epsilon(\cdot,t), U_s\Psi_\epsilon(\cdot,t)\Big\rangle \\ + 2\mathrm{Re}\langle U_b\Psi_\epsilon(\cdot,t), U_s\Psi_\epsilon(\cdot,t)\rangle + \|U_s\Psi_\epsilon(\cdot,t)\|^2\Big) \le const. \tag{54}$$

Using the positivity of U_s and (53), the third term satisfies

$$\sup_{t\in\mathbb{R}} |2\mathrm{Re}\langle U_b\Psi_\epsilon(\cdot,t), U_s\Psi_\epsilon(\cdot,t)\rangle| \le 2\|U_b\|_\infty \sup_{t\in\mathbb{R}} |\langle \Psi_\epsilon(\cdot,t), U_s\Psi_\epsilon(\cdot,t)\rangle| \le const. \tag{55}$$

The key point now is the following claim:

$$\mathrm{Re}\langle -\Delta\psi, U_s\psi\rangle \ge 0 \quad \text{for } \psi \in \mathrm{H}^2(\mathbb{R}^d). \tag{56}$$

Postponing its proof, substitution of (55), (56) (with $\psi = \Psi_\epsilon(\cdot,t)$) into (54) yields

$$\sup_{t\in\mathbb{R}} \Big\| \Big(-\frac{\epsilon^2}{2}\Delta + U_b\Big)\Psi_\epsilon(\cdot,t)\Big\|^2 \le const., \quad \sup_{t\in\mathbb{R}} \|U_s\Psi_\epsilon(\cdot,t)\|^2 \le const.,$$

establishing the assertion.

It remains to prove (56). (This depends on the Coulombic nature of U_s as well as the fact that it is positive, i.e., repulsive.) By a standard approximation argument, using the density of $\mathrm{C}_0^\infty(\mathbb{R}^d)$ in $\mathrm{H}^2(\mathbb{R}^d)$ and the fact that, by Hardy's inequality, $\psi \mapsto U_s\psi$ is a continuous map from $\mathrm{H}^1(\mathbb{R}^d)$ to $\mathrm{L}^2(\mathbb{R}^d)$, it suffices to prove (56) for $\psi \in \mathrm{C}_0^\infty(\mathbb{R}^d)$. In this case, compute

$$\mathrm{Re}\langle -\Delta\psi, U_s\psi\rangle = \mathrm{Re}\int_{\mathbb{R}^d} \nabla\overline{\psi}\cdot\nabla(U_s\psi) = \int_{\mathbb{R}^d} |\nabla\psi|^2 U_s + \mathrm{Re}\int_{\mathbb{R}^d} (\nabla\overline{\psi})\psi\cdot\nabla U_s.$$

The first term is ≥ 0 and the second term equals

$$\frac{1}{2}\int_{\mathbb{R}^d}\big((\nabla\overline{\psi})\psi+\overline{\psi}\nabla\psi\big)\cdot\nabla U_s=\frac{1}{2}\int_{\mathbb{R}^d}\nabla|\psi|^2\cdot\nabla U_s=\frac{1}{2}\int_{\mathbb{R}^d}|\psi|^2(-\Delta U_s).$$

Now, considering e.g. the term $\frac{1}{|R_1-R_2|}$ in U_s, cf. (7), write

$$-\Delta_{(R_1,\dots,R_M)}=-\Delta_{\frac{R_1+R_2}{\sqrt{2}}}-\Delta_{\frac{R_1-R_2}{\sqrt{2}}}-\Delta_{(R_3,\dots,R_M)}$$

and hence

$$-\Delta_{(R_1,\dots,R_M)}\frac{1}{|R_1-R_2|}=-2\Delta_{R_1-R_2}\frac{1}{|R_1-R_2|}=8\pi\delta(R_1-R_2)$$

(recall $-\Delta\frac{1}{|\cdot|}=4\pi\delta$ in $\mathbb{R}^3$). Thus $\int_{\mathbb{R}^d}|\psi|^2(-\Delta U_s)\geq 0$, which completes the proof of (56). □

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