Technische Universität München
Department of Mathematics

Evolution of Angular Momentum Expectation in Quantum Mechanics

Bachelor's Thesis by Thomas Wiatowski

supervisor : Prof. Dr. Gero Friesecke
academic advisor : Dipl.-Math. Mario Koppen
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Ich erkläre hiermit, daß ich die Bachelorarbeit selbständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

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Abstract

A mathematically rigorous derivation of the evolution of angular momentum expectation value is given, under assumptions which include Hamiltonians with potential wells.

Die Zeitentwicklung des Erwartungswertes des Drehimpulses wird mathematisch exakt hergeleitet, unter Annahmen, die Hamilton Operatoren mit Potentialtöpfen beinhalten.

Introduction

In classical mechanics, the time evolution of position, momentum and other observables $f = f(q,p)$ is given by

$$\frac{d}{dt}f(q,p) = -\frac{\partial f}{\partial p}\frac{\partial H}{\partial q} + \frac{\partial f}{\partial q}\frac{\partial H}{\partial p} =: \{H, f\},$$

where $H = H(q,p)$ is the Hamiltonian of the system and (q,p) are the canonical coordinates on the phase space. In contrast to quantum physics, the classical theory considers observables as values of real-valued functions on phase space, and not as spectral values of self-adjoint operators on a Hilbert space. When quantizing the classical concept of the time evolution of observables, we are concerned with the quantum mechanical analogy – Ehrenfest's theorem [Ehr27]. This well known result relates the time derivative of the expectation value for a quantum mechanical operator A to the Hamiltonian H of the system as follows

$$\frac{d}{dt}\langle A\rangle_{\psi(t)} = i\langle[H, A]\rangle_{\psi(t)}.$$

Heuristic justifications can be found in any text book on quantum mechanics. They make mathematically sense when A and H are bounded, but realistic quantum Hamiltonians and observables are unbounded and only defined on dense domains. A mathematically rigorous derivation of Ehrenfest's equation for the evolution of position and momentum expectation values is given by [FK09], proving

$$\frac{d}{dt}\langle X_{i_j}\rangle_{\psi(t)} = \frac{1}{m_{i_j}}\langle P_{i_j}\rangle_{\psi(t)} \qquad \text{and} \qquad \frac{d}{dt}\langle P_{i_j}\rangle_{\psi(t)} = \langle -\frac{\partial V}{\partial x_{i_j}}\rangle_{\psi(t)}$$

under general and natural assumptions on the Hamiltonian which include atomic and molecular Hamiltonians with Coulomb interaction.

Due to the fact that these equations are of Newtonian form, i.e. the mean values of position and momentum operator correspond to Newton's second law of motion, it is natural to make a similar assumption about the angular momentum operator. The main purpose of this thesis is to derive rigorously an Ehrenfest equation for the angular momentum expectation, which is, to the best of my knowledge, so far missing from the literature. We prove

$$\frac{d}{dt}\langle L_{i_j}\rangle_{\psi(t)} = \langle -(X_{i\bullet} \wedge \nabla_i V)_j\rangle_{\psi(t)}$$

under assumptions which include Hamiltonians with potential wells.

The plan of this thesis is as follows: in section one mathematical concepts of quantum mechanics are introduced, including the analysis of operators on the Hilbert space $L^2(\mathbb{R}^{3n})$, which are essential for discussions in quantum mechanics. The second section provides the framework for the derivation of the evolution of angular momentum expectation value and presents the main result of this thesis, Theorem 2.3.1, which is proved in the third section by functional analytic methods. The last chapter deals with a short interpretation of the results and illustrates an application to Hamiltonians with potential wells and rotationally symmetric potentials.

Contents

1 Mathematical Concepts of Quantum Mechanics

1.1 Wave functions and state space

In quantum mechanics, the *state* of a particle is described by a complex-valued function (called *wave function*) of position and time, $\psi : \mathbb{R}^3 \times [0, \infty) \to \mathbb{C}$, where all functions that are scalar multiples of ψ describe the same state as ψ. To describe the state of a quantum system of n particles at a certain time t, superposition of n wave functions of those n particles leads to a complex-valued function, $\psi : \mathbb{R}^{3n} \times [0, \infty) \to \mathbb{C}$ – the wave function of the quantum system in $\mathbb{R}^{3n}$. Motivated by the well known "double-slit experiment", it is required that $|\psi(\cdot, t)|^2$ is the probability distribution for the particles' position, x, at time t. That is, the probability that n particles are in the region $\Omega \subset \mathbb{R}^{3n}$ at time t is $\int_\Omega |\psi(x, t)|^2 dx$. Thus the normalization $\int_{\mathbb{R}^{3n}} |\psi(x, t)|^2 dx = 1$ is required.
The space of all possible states of n particles at a given time is called the *state space*, which is here the space of square-integrable functions

$$L^2(\mathbb{R}^{3n}) := \{\psi : \mathbb{R}^{3n} \to \mathbb{C} \mid \int_{\mathbb{R}^{3n}} |\psi(x)|^2 dx < \infty\}.$$

In fact, it is a *Hilbert space* with *inner product* given by $\langle \psi, \phi \rangle := \int_{\mathbb{R}^{3n}} \overline{\psi(x)} \phi(x) dx$. Here, and in what follows, the notation $\| \cdot \|_{L^2}$ is used for $\| \cdot \|_{L^2(\mathbb{R}^{3n})} := \sqrt{\langle \cdot, \cdot \rangle}$. Due to the fact that scalar multiples of an element of $L^2(\mathbb{R}^{3n})$ describe the same state as the element itself, one-dimensional subspaces in $L^2(\mathbb{R}^{3n})$ are associated with the *states of the system.*

1.2 Operators on the Hilbert space $L^2(\mathbb{R}^{3n})$

As outlined above, the space of quantum mechanical states of a system is a Hilbert space. The theory of operators on a Hilbert space provides the mathematical framework of quantum mechanics, so it is inevitable to study them. A *linear operator* A on the Hilbert space $L^2(\mathbb{R}^{3n})$ is a map from $L^2(\mathbb{R}^{3n})$ to itself, satisfying the *linearity property* $A(\alpha\psi + \beta\phi) = \alpha A(\psi) + \beta A(\phi)$ for $\alpha, \beta \in \mathbb{C},\ \psi, \phi \in L^2(\mathbb{R}^{3n})$. For functional analytic motives, an operator A is required to be defined only on a dense *domain*, i.e. $\overline{D(A)}^{\| \cdot \|_{L^2}} = L^2(\mathbb{R}^{3n})$, where the set $D(A) := \{\psi \in L^2(\mathbb{R}^{3n}) \mid A\psi \in L^2(\mathbb{R}^{3n})\}$ is called the domain of A. An example of a dense subset of $L^2(\mathbb{R}^{3n})$ is $C_0^\infty(\mathbb{R}^{3n})$, the *infinitely often differentiable functions with compact support* (for the proof, see [Eva10b]). The domain $D(A)$ is dense in $L^2(\mathbb{R}^{3n})$ if it contains $C_0^\infty(\mathbb{R}^{3n})$.

It is notable that every operator defined in this thesis satisfies the linearity property. We focus not only on linearity property, but also on several other ones, defined as follows:

Definition 1.2.1 (operator properties)
Let A be a densely defined operator on $D(A) \subset L^2(\mathbb{R}^{3n})$. Then

(i) A is *continuous* if for every sequence $\{\psi_n\}_{n\in\mathbb{N}} \subset D(A)$ converging to $\psi \in L^2(\mathbb{R}^{3n})$ one has
$$\lim_{n\to\infty} A\psi_n = A\psi.$$

(ii) A is *bounded* if $\|A\phi\|_{L^2} \leq C\|\phi\|_{L^2}$ for all $\phi \in L^2(\mathbb{R}^{3n})$.

(iii) A is *bounded on* $S \subset L^2(\mathbb{R}^{3n})$ if $\|A\phi\|_{L^2} \leq C_S\|\phi\|_{L^2}$ for all $\phi \in S$.

(iv) A is *closed* if for every sequence $\{\psi_n\}_{n\in\mathbb{N}} \subset D(A)$ converging to $\psi \in L^2(\mathbb{R}^{3n})$ such that $A\psi_n \to \phi \in L^2(\mathbb{R}^{3n})$ as $n \to \infty$ one has
$$\psi \in D(A) \text{ and } A\psi = \phi.$$

(v) A is *symmetric* if for all $\psi, \phi \in D(A) : \langle A\psi, \phi\rangle = \langle \psi, A\phi\rangle$.

(vi) The *adjoint* of the operator A is the operator A^* satisfying
$$\langle A^*\psi, \phi\rangle = \langle \psi, A\phi\rangle$$
for all $\phi \in D(A)$, for ψ in the domain
$$\begin{aligned} D(A^*) :&= \{\psi \in L^2(\mathbb{R}^{3n}) \mid \phi \mapsto \langle \psi, A\phi\rangle \text{ is continuous on } D(A)\} \\ &= \{\psi \in L^2(\mathbb{R}^{3n}) \mid |\langle \psi, A\phi\rangle| \leq C_{D(A),\psi}\|\phi\|_{L^2}\ \forall\ \phi \in D(A)\}. \end{aligned}$$
Further A is *self-adjoint* if $A = A^*$ (i.e. $D(A) = D(A^*)$ and $Ax = A^*x$ for all $x \in D(A)$).

□

It is important to mention that for linear operators, the elementary concepts of "boundedness" and "continuity" are equivalent (for the proof, see [Wer00a]). Furthermore, every self-adjoint operator is by definition symmetric. And if $D(A) = L^2(\mathbb{R}^{3n})$, then every bounded operator is closed. The next lemma is useful for extensions of bounded operators on dense domains and the connection between bounded, symmetric operators and self-adjoint ones.

Lemma 1.2.2
Let A be a densely defined operator on $D(A) \subset L^2(\mathbb{R}^{3n})$.

(i) If A is bounded on its domain $D(A)$, i.e. $\|A\psi\|_{L^2} \leq C_{D(A)}\|\psi\|_{L^2}$ for all $\psi \in D(A)$, then it extends to a bounded operator (also denoted A) on $L^2(\mathbb{R}^{3n})$, satisfying the same bound, $\|A\psi\|_{L^2} \leq C_{D(A)}\|\psi\|_{L^2}$ for all $\psi \in L^2(\mathbb{R}^{3n})$.

(ii) If A is bounded and symmetric then it is self-adjoint.

Proof:

ad (i) As $D(A)$ is dense in $L^2(\mathbb{R}^{3n})$, for any $\psi \in L^2(\mathbb{R}^{3n})$ there is a sequence $\{\psi_n\}_{n\in\mathbb{N}} \subset D(A)$ such that $\psi_n \to \psi$ in L^2 as $n \to \infty$. As a convergent sequence, $\{\psi_n\}_{n\in\mathbb{N}}$ is a Cauchy sequence. Then the relation $\|A\psi_n - A\psi_m\|_{L^2} \leq C_{D(A)}\|\psi_n - \psi_m\|_{L^2}$ shows that $\{A\psi_n\}_{n\in\mathbb{N}} \subset L^2(\mathbb{R}^{3n})$ is a Cauchy sequence as well, so $A\psi_n \to \phi$ in L^2, for some $\phi \in L^2(\mathbb{R}^{3n})$ (by completeness of $L^2(\mathbb{R}^{3n})$). Setting $A\psi := \phi$, this extends A to a bounded operator on $L^2(\mathbb{R}^{3n})$ with the same constant $C_{D(A)}$, because

$$\|A\psi\|_{L^2} = \|\phi\|_{L^2} = \lim_{n\to\infty} \|A\psi_n\|_{L^2} \leq \lim_{n\to\infty} C_{D(A)}\|\psi_n\|_{L^2} = C_{D(A)}\|\psi\|_{L^2},$$

by continuity of the norm.

ad (ii) Since A is bounded, by Definition 1.2.1(i) A is well-defined on $L^2(\mathbb{R}^{3n})$. By Lemma 1.2.2(i) we may extend A to a bounded operator with $D(A) = L^2(\mathbb{R}^{3n})$. Since (using the Cauchy Schwartz inequality)

$$|\langle\psi, A\phi\rangle| \leq \|\psi\|_{L^2} C_{D(A)}\|\phi\|_{L^2} \leq C_{D(A),\psi}\|\phi\|_{L^2}$$

for $\psi, \phi \in L^2(\mathbb{R}^{3n})$, we have $D(A^*) = L^2(\mathbb{R}^{3n})$, so it follows $D(A) = D(A^*)$. Hence, A is self-adjoint.

■

Motivated by Lemma 1.2.2(i), we assume of a bounded operator A that its domain $D(A)$ equals $L^2(\mathbb{R}^{3n})$. The following operators play an important role for our further considerations; because of that, they are analysed in terms of the properties stated in the Definition 1.2.1.

Example 1.2.3

(i) *Multiplication operator*: Let $V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R})$ and denote by the same letter V the linear operator "multiplying by V", that is $(V\psi)(x) := V(x)\psi(x)$. Defining V on the domain $L^2(\mathbb{R}^{3n})$, this multiplication operator is well-defined, since $V\psi \in L^2(\mathbb{R}^{3n})$ for $\psi \in L^2(\mathbb{R}^{3n})$ as $\|V\psi\|_{L^2} \leq \|V\|_{L^\infty}\|\psi\|_{L^2} < \infty$. This proves the continuity of V (with bound $C_V := \|V\|_{L^\infty}$).
V is real-valued and hence $\langle V\psi, \phi\rangle = \langle\psi, V\phi\rangle$ for all $\psi,\ \phi \in L^2(\mathbb{R}^{3n})$. Since the integral $\int_{\mathbb{R}^{3n}} V(x)\overline{\psi(x)}\phi(x)dx$ converges (using the Cauchy Schwarz inequality and boundedness of V), it follows that V is symmetric. Due to the fact that V is bounded and symmetric, it follows from Lemma 1.2.2(ii) that V is self-adjoint.

(ii) *Laplace operator*: Let $\triangle := \sum_{i=1}^{n}\sum_{j=1}^{3} \partial^2/\partial x_{i_j}^2$ be the Laplace operator ("Laplacian"). $\triangle$ is naturally well-defined on the Sobolev space of second order,

$$D(\triangle) := H^2(\mathbb{R}^{3n}) := \{\psi \in L^1_{loc}(\mathbb{R}^{3n}) \mid \partial^\alpha\psi \in L^2(\mathbb{R}^{3n}) \ \forall\ \alpha \in \mathbb{N}_0^{3n}, |\alpha|_1 \leq 2\},$$

where $\partial^\alpha := \frac{\partial^{|\alpha|_1}}{\partial^{\alpha_{1_1}} x_{1_1} \dots \partial^{\alpha_{n_3}} x_{n_3}}$ with $|\alpha|_1 := \sum_{i=1}^{n}\sum_{j=1}^{3} |\alpha_{i_j}|$. It is obvious that $C_0^\infty(\mathbb{R}^{3n}) \subset H^2(\mathbb{R}^{3n})$, hence the operator is densely defined. For completeness, the H^2*-norm* is defined as follows (for the proof that this is a norm on $H^2(\mathbb{R}^{3n})$, see e.g. [Eva10b]):

$$\|\psi\|_{H^2(\mathbb{R}^{3n})} := \left(\sum_{|\alpha|_1\leq 2} \|\partial^\alpha\psi\|_{L^2}^2\right)^{\frac{1}{2}}.$$

If $\psi \in H^2(\mathbb{R}^{3n})$, then $(\widehat{\triangle\psi})(k) = -\|k\|_2^2\hat{\psi}(k)$ and $\|k\|_2^2\hat{\psi} \in L^2(\mathbb{R}^{3n})$ (using Fourier transforms, see e.g. [Wer00b]). Here, $\|\cdot\|_2$ stands for the Euclidean norm on $\mathbb{R}^{3n}$. $\triangle$ is symmetric on $H^2(\mathbb{R}^{3n})$, since (using Plancherel's theorem, see e.g. [Wer00b]) for any ψ, $\phi \in H^2(\mathbb{R}^{3n})$

$$\langle\triangle\psi, \phi\rangle = -\int_{\mathbb{R}^{3n}} \overline{\|k\|_2^2\hat{\psi}(k)}\hat{\phi}(k)dk = -\int_{\mathbb{R}^{3n}} \overline{\hat{\psi}(k)}\|k\|_2^2\hat{\phi}(k)dk = \langle\psi, \triangle\phi\rangle$$

and the fact that both integrals converge using again the Cauchy Schwartz inequality. For the proof of self-adjointness of $\triangle$ on $H^2(\mathbb{R}^{3n})$, see [HS96b], and for an example that differential operators are usually unbounded on $L^2(\mathbb{R}^{3n})$, see [Wer00c].

(iii) *Position operator*: Let $X : \mathbb{R}^{3n} \to \mathbb{R}^{3n}, x \mapsto x$ and – in analogy to the multiplication operator V– denote by the same letter X the linear operator "multiplying by X", that is $(X\psi)(x) := x\psi(x)$. The operator X is well-defined on the domain

$$D(X) := \{\psi \in L^2(\mathbb{R}^{3n}) \mid \int_{\mathbb{R}^{3n}} \|x\|_2^2|\psi(x)|^2dx < \infty\}.$$

Using the same arguments as in (i), applied to integrals with vector valued integrands, it is straightforward to show that X is symmetric on $D(X)$.
Similar analysis leads to the symmetry of the *coordinate multiplication operator* $X_{i_j} : \mathbb{R}^{3n} \to \mathbb{R}$, $x \mapsto x_{i_j}$ on the domain

$$D(X_{i_j}) := \{\psi \in L^2(\mathbb{R}^{3n}) \mid \int_{\mathbb{R}^{3n}} |x_{i_j}\psi(x)|^2dx < \infty\}.$$

$D(X_{i_j})$ contains $C_0^\infty(\mathbb{R}^{3n})$, hence it is dense in $L^2(\mathbb{R}^{3n})$. Further, X_{i_j} is unbounded on $L^2(\mathbb{R}^{3n})$, which can be shown with the function

$$\psi(x) = \frac{1}{(1 + \|x\|_2^2)^{\frac{3n+1}{4}}},$$

i.e., $\psi \in L^2(\mathbb{R}^{3n})$ but $X_{i_j}\psi \notin L^2(\mathbb{R}^{3n})$.

(iv) *Momentum operator*: Let $P_{i_j} := -i\partial/\partial x_{i_j}$ on $L^2(\mathbb{R}^{3n})$ with domain

$$D(P_{i_j}) := \{\psi \in L^2(\mathbb{R}^{3n}) \mid \int_{\mathbb{R}^{3n}} |k_{i_j}\hat{\psi}(k)|^2 dk < \infty\}$$

be the j^{th} component of the momentum operator of the i^{th} particle (for convenience the focus is on components of particle's momentum operator, rather than on the whole momentum operator $P := -i\nabla$). If $\psi \in D(P_{i_j})$, then $\widehat{P_{i_j}\psi}(k) = k_{i_j}\hat{\psi}(k)$ and $k_{i_j}\hat{\psi} \in L^2(\mathbb{R}^{3n})$, so it is obvious that P_{i_j} is well-defined on $D(P_{i_j})$. Again, it is not hard to prove that $C_0^\infty(\mathbb{R}^{3n}) \subset D(P_{i_j})$, so the operator is densely defined. P_{i_j} is symmetric on $D(P_{i_j})$, since (again using Plancherel's theorem) for any ψ, $\phi \in D(P_{i_j})$

$$\langle P_{i_j}\psi, \phi\rangle = \int_{\mathbb{R}^{3n}} \overline{k_{i_j}\hat{\psi}(k)}\hat{\phi}(k)dk = \int_{\mathbb{R}^{3n}} \overline{\hat{\psi}(k)}k_{i_j}\hat{\phi}(k)dk = \langle\psi, P_{i_j}\phi\rangle$$

and the fact that both integrals converge using again the Cauchy Schwartz inequality. Analogue to (ii), differential operators are usually unbounded on $L^2(\mathbb{R}^{3n})$.

Having analysed various symmetric and self-adjoint operators, the following definition is mentioned for completeness.

Definition 1.2.4 (observable)
An *observable* is a densely defined symmetric operator on the state space $L^2(\mathbb{R}^{3n})$.

□

1.3 Evolution of wave function

Not only is it interesting to know the state of n particles at a given time, but also to focus on the time evolution of the particles' wave function. The equation which governs the evolution of particles' wave function is called the *Schrödinger equation* and can be written as

$$\frac{\partial}{\partial t}\psi = -iH\psi, \tag{1}$$

where the linear operator H, given by

$$H := -\sum_{i=1}^{n}\sum_{j=1}^{3}\frac{m_{i_j}}{2}\frac{\partial^2}{\partial x_{i_j}^2} + V, \tag{2}$$

is called the *Hamiltonian*, acting on $D(H) \subset L^2(\mathbb{R}^{3n})$ (for well-definedness and dense domain, see section 1.5). Here a physical system is considered, consisting of n particles of masses $m_1, ..., m_n$ which interact via the potential V. All information about a quantum mechanical system (atoms, molecules, nuclei, solids, etc.) is contained in the Hamiltonian for the system. Supplementing equation (1) with the initial condition $\psi|_{t=0} = \psi_0$, for some $\psi_0 \in L^2(\mathbb{R}^{3n})$, the initial value problem

$$\frac{\partial}{\partial t}\psi = -iH\psi, \quad \psi|_{t=0} = \psi_0 \tag{3}$$

is called the *Cauchy problem*. It is far from obvious that both existence and uniqueness of solutions of the Cauchy problem do not depend on the particular form of the operator H, but rather follow from the self-adjointness property of the Hamiltonian.

But firstly it is not clear, under which assumptions H is a self-adjoint operator. And secondly, we do not know anything about the fact, whether self-adjointness of H is already sufficient for uniqueness and existence of solutions of the Cauchy problem (3). The introduction of strongly continuous one-parameter unitary groups helps for the latter.

1.4 Strongly continuous one-parameter unitary groups

Definition 1.4.1 (strongly continuous one-parameter unitary groups)
A one-parameter family of bounded, linear operators $(T_t|\ t \in \mathbb{R})$ on $L^2(\mathbb{R}^{3n})$ is called *strongly continuous one-parameter unitary group* if

(i) $T_0 = Id$

(ii) $T_{s+t} = T_s T_t$ for all $s, t \in \mathbb{R}$

(iii) $\lim_{t\to 0} T_t x = x$ for all $x \in L^2(\mathbb{R}^{3n})$

(iv) T_t is unitary for all $t \in \mathbb{R}$ (i.e. $T_t T_t^* = T_t^* T_t = Id$).

The *generator* of such a strongly continuous one-parameter unitary group is the following operator

$$Ax = \lim_{h\to 0} \frac{T_h x - x}{h}$$

on the domain

$$D(A) := \{x \in L^2(\mathbb{R}^{3n})\ |\ \lim_{h\to 0} \frac{T_h x - x}{h} \text{ exists}\}.$$

□

Due to the fact that $0 \in D(A)$, every strongly continuous one-parameter unitary group has a generator with non-empty domain. The notation $T_t x =: e^{tA}x$ is pretty helpful as we will see in the Theorem 1.4.4 about solutions of the abstract Cauchy problem.

Remark: In fact, this notation could be misleading when thinking about the definition of the exponential power series for bounded operators A. But in general, the generator is a unbounded operator, hence the definition by power must not be used.

The following lemma deals with further properties of the generator.

Lemma 1.4.2
Let A be the generator of a strongly continuous one-parameter unitary group $(e^{tA} \mid t \in \mathbb{R})$ on $L^2(\mathbb{R}^{3n})$. Let $t \in \mathbb{R}$, then

(i) $e^{tA}(D(A)) \subset D(A)$.

(ii) $e^{tA}Ax = Ae^{tA}x$ for all $x \in D(A)$.

(iii) A is densely defined, i.e. $\overline{D(A)}^{\|\cdot\|_{L^2}} = L^2(\mathbb{R}^{3n})$.

Proof: See [Wer00c].

■

We recall here two frequently used facts about strongly continuous one-parameter unitary groups, which are helpful for solving the Cauchy problem (3).

Lemma 1.4.3 (Stone's theorem on one-parameter unitary groups)
Let $(T_t \mid t \in \mathbb{R})$ be a strongly continuous one-parameter unitary group on $L^2(\mathbb{R}^{3n})$. Then there exists a unique self-adjoint operator A such that $T_t = e^{itA}$, $t \in \mathbb{R}$. Conversely, let A be a self-adjoint operator on $L^2(\mathbb{R}^{3n})$, then $T_t := e^{itA}$, $t \in \mathbb{R}$, is a strongly continuous one-parameter family of unitary operators.

Proof: See [Sto32].

■

Theorem 1.4.4 (solution of the abstract Cauchy problem)
Let A be the generator of a strongly continuous one-parameter unitary group $(e^{tA} \mid t \in \mathbb{R})$ on $L^2(\mathbb{R}^{3n})$, $x_0 \in D(A)$. Define $u : \mathbb{R} \to L^2(\mathbb{R}^{3n})$, $u(t) = e^{tA}x_0$. Then u is continuously differentiable, $u(\mathbb{R}) \subset D(A)$ and the unique solution of the *abstract Cauchy problem*

$$u' = Au,\ u(0) = x_0.$$

Proof: See [Wer00c].

■

Having quoted some results on the analysis of strongly continuous one-parameter unitary groups, the Cauchy problem (3) for a self-adjoint Hamiltonian can be solved. In addition, important properties used in this thesis are outlined in the following corollary.

Corollary 1.4.5
Let $H : D(H) \to L^2(\mathbb{R}^{3n})$ be a self-adjoint Hamiltonian of form (2). For $\psi_0 \in D(H)$, define $\psi(t) := e^{-itH}\psi_0$. Then

(i) $t \mapsto \psi(t)$ is a continuously differentiable map from $\mathbb{R}$ to $L^2(\mathbb{R}^{3n})$ and is the unique solution of the Cauchy problem (3).

(ii) e^{-itH} leaves $D(H)$ invariant, i.e. $e^{-itH}(D(H)) \subset D(H)$, and commutes on $D(H)$ with H.

(iii) $\|\psi(t)\|_{L^2}$ and$\|H\psi(t)\|_{L^2}$ are *conserved quantities*, i.e.

$$\|\psi(t)\|_{L^2} = \|\psi_0\|_{L^2}$$

and

$$\|H\psi(t)\|_{L^2} = \|H\psi_0\|_{L^2}$$

for all $t \in \mathbb{R}$.

Proof: (i) follows directly from Lemma 1.4.3 and Theorem 1.4.4, since $-H$ is again a self-adjoint operator. Lemma 1.4.2 leads to (ii). Unitarity of e^{-itH} and (ii) yield (iii), since unitary operators U are isometries, as follows from $\langle U\psi, U\psi\rangle = \langle \psi, U^*U\psi\rangle = \langle \psi, \psi\rangle$ for all $\psi \in D(U)$.

■

We conclude this section by emphasizing that for Schrödinger equation formulation of quantum mechanics to make sense, the Hamiltonian must be self-adjoint. We will focus the important question of which properties of the Hamiltonian H give rise to self-adjointness in the next chapter.

1.5 Hamilton operator

As outlined in section 1.3, the Hamilton operator

$$H := -\sum_{i=1}^{n}\sum_{j=1}^{3} \frac{m_{i_j}}{2}\frac{\partial^2}{\partial x_{i_j}^2} + V$$

enters the Schrödinger equation governing the evolution of states. Since H is an operator, it is a map $H : D(H) \to L^2(\mathbb{R}^{3n})$. For convenience we write $H = -\frac{1}{2}\triangle + V$, where the potential $V : \mathbb{R}^{3n} \to \mathbb{R}$ acts by multiplication. So far, it is not obvious for which domain $D(H)$ the operator H is well-defined or even self-adjoint. The target in this section is to focus on requirements on V, which lead to self-adjointness of H. According to our considerations in section 1.2, the precise meaning of the statement "the operator H is self-adjoint" is as follows: there is a domain $D(H)$, with $C_0^\infty(\mathbb{R}^{3n}) \subset D(H) \subset L^2(\mathbb{R}^{3n})$, for which H is self-adjoint. The exact form of $D(H)$ depends on V.

Identifying $H = -\frac{1}{2}\triangle + V$ as a sum of two operators $A = -\frac{1}{2}\triangle$ and $B = V$ with certain domains $D(A)$ and $D(B)$, now the following question is studied. Suppose A is self-adjoint and B is a symmetric operator such that $D(A) \cap D(B)$ is dense in $L^2(\mathbb{R}^{3n})$; what conditions does B have to satisfy in order that $A + B$ is self-adjoint? This question will be answered in a very satisfactory manner by the Kato-Rellich theorem 1.5.2, which forms the basic tool for proving self-adjointness of Hamiltonians. But to apply the Kato-Rellich theorem, we have to define the relatively bounded operators.

Definition 1.5.1 (relatively bounded operator)
Let A be a densely defined self-adjoint operator on $D(A) \subset L^2(\mathbb{R}^{3n})$ and B be a densely defined symmetric operator on $D(B) \subset L^2(\mathbb{R}^{3n})$ with $D(A) \subset D(B)$. *B is A- bounded with relative bound α* if there are positive constants α, β such that

$$\|B\psi\|_{L^2} \leq \alpha \|A\psi\|_{L^2} + \beta \|\psi\|_{L^2}$$

for all $\psi \in D(A)$.

□

It is obvious, but important to note, that any bounded operator B is A- bounded for any linear operator A with relative bound $\alpha = 0$.

Theorem 1.5.2 (the Kato-Rellich theorem)
Let A be a densely defined self-adjoint operator on $D(A) \subset L^2(\mathbb{R}^{3n})$ and B be a densely defined, closed, symmetric, A-bounded operator with relative bound $\alpha < 1$ on $D(B) \subset L^2(\mathbb{R}^{3n})$ with $D(A) \subset D(B)$. Then $A + B$ is self-adjoint on $D(A)$.

Proof: See [HS96c].

■

An interesting interpretation of the Kato-Rellich theorem is the following: H is considered as a perturbation of $-\frac{1}{2}\triangle$ by the potential V. Considering the problem in *perturbation theory*, which potentials V preserve the self-adjointness of $-\frac{1}{2}\triangle$, the Kato-Rellich theorem says that for any sufficiently regular V that is small relative to $-\frac{1}{2}\triangle$ in a certain sense, the resulting Hamiltonian is again self-adjoint. For interesting discussions in the mathematics literature, see e.g. [HS96a].

As a consequence, the Kato-Rellich theorem can be applied to the following situation.

Corollary 1.5.3
Let $V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R})$ be the multiplication operator with $D(V) = L^2(\mathbb{R}^{3n})$. Then the operator $H = -\frac{1}{2}\triangle + V$, defined on $D(\triangle) = H^2(\mathbb{R}^{3n})$, is self-adjoint.

Proof: This is an immediate consequence of Example 1.2.3(i),(ii) and the Kato-Rellich theorem. Since V is bounded on $L^2(\mathbb{R}^{3n})$, V is a $-\frac{1}{2}\triangle$- bounded operator with relative bound $\alpha = 0$. Further V is closed and symmetric and $\triangle$ is self-adjoint on $H^2(\mathbb{R}^{3n})$. Scaling a self-adjoint operator by a constant different from zero does not change the self-adjointness property. Hence, $-\frac{1}{2}\triangle$ is again self-adjoint. The Kato-Rellich theorem yields the assertion.

■

As mentioned in Corollary 1.4.5, the abstract Cauchy problem (3) can be solved in the situation of Corollary 1.5.3. In fact, the requirement on V to be an element of $L^\infty(\mathbb{R}^{3n}, \mathbb{R})$ with the condition that ∇V is an element of $L^\infty(\mathbb{R}^{3n}, \mathbb{R}^{3n})$ forms the main setting in this thesis. But before concentrating on this situation, the focus is on mean values and commutators of operators.

1.6 Mean values and commutators

We recall that in quantum mechanics, the probability distribution for the position, x, of n particles at a given time t, is $|\psi(\cdot, t)|^2$. According to that, the mean value of the position at time t is given by $\int_{\mathbb{R}^{3n}} x|\psi(x,t)|^2 dx$ (note that this is a vector in $\mathbb{R}^{3n}$). Applying this to the coordinate multiplication operator (see Example 1.2.3), $\langle \psi, x_{i_j}\psi\rangle$ is the mean value of the j^{th} component of the i^{th} particle's coordinate $x_{i\bullet} \in \mathbb{R}^3$ in the state $\psi \in D(X_{i_j})$. Motivated by this, the mean value for a general linear operator is defined as follows.

Definition 1.6.1 (mean value)
Let A be a densely defined operator on $D(A) \subset L^2(\mathbb{R}^{3n})$. The *mean value* of A in the state $\psi \in D(A)$ is

$$\langle A\rangle_\psi := \langle \psi, A\psi\rangle.$$

□

It is notable that the mean value $\langle A\rangle_\psi$ exists for all $\psi \in D(A)$, since

$$|\langle \psi, A\psi\rangle| \leq \|\psi\|_{L^2}\|A\psi\|_{L^2} < \infty.$$

Due to the fact that the composition of two linear operators is generally not commutative, the next definition is quite useful.

Definition 1.6.2 (commutator)
Let A and B be two bounded operators on $L^2(\mathbb{R}^{3n})$. Then the *commutator* $[A, B]$ is the operator defined by

$$[A, B] := AB - BA, \qquad D([A, B]) := L^2(\mathbb{R}^{3n}).$$

□

Again, it should be noted that the commutator of two bounded operators is well-defined, since for any $\psi \in L^2(\mathbb{R}^{3n})$

$$\|[A,B]\psi\|_{L^2} \leq \|AB\psi\|_{L^2} + \|BA\psi\|_{L^2} \leq C_1\|B\psi\|_{L^2} + C_2\|A\psi\|_{L^2} \leq 2C_1C_2\|\psi\|_{L^2} \ < \infty,$$

with C_1, C_2 boundedness constants of A and B. But defining the commutator of two operators when at least one of them is unbounded requires caution, due to domain considerations. Of course, when ψ belongs to the smaller set $D(AB) \cap D(BA)$, where $D(AB) := \{\psi \in D(B) \mid B\psi \in D(A)\}$, the commutator, even for unbounded operators, is well-defined. But this domain does not need to be dense in $L^2(\mathbb{R}^{3n})$. An interesting basic example from physics about the "domain problem" is explained in Example 1.6.5 at the end of this section. But before concentrating on this "domain problem", the focus is on basic commutator properties and commutator examples.

Lemma 1.6.3
Let A, B and C be three bounded operators on $L^2(\mathbb{R}^{3n})$, then the commutator $[\cdot,\cdot]$ has the following properties:

- *antisymmetric*, i.e. $[A,B] = -[B,A]$.
- *linear*, i.e. $[\lambda A + B, C] = \lambda[A,C] + [B,C]$ for all $\lambda \in \mathbb{C}$.
- *product rule*, i.e. $[A,BC] = [A,B]C + B[A,C]$.
- *unbounded case*, i.e. if at least one of the operators A, B or C is unbounded, properties (i)–(iii) are still applicable to the domain

$$D(AB) \cap D(BA) \qquad \text{or} \qquad \bigcap_{X,Y \in \{A,B,C\}} D(XY).$$

Proof: These properties follow from elementary calculations. We omit them here.

■

It is often useful to compute the commutator of two unbounded operators just for functions in $C_0^\infty(\mathbb{R}^{3n})$, which is done in the next Example 1.6.4. To extend the analysis to functions not contained in $C_0^\infty(\mathbb{R}^{3n})$, a lot of care is needed. A good example for such an extension can be found in the proof of Theorem 2.3.1 b).

Example 1.6.4
Let X_{i_j}, P_{i_j} be defined as in Example 1.2.3(iii),(iv) and $H = -\frac{1}{2}\triangle + V$ with $V \in L^\infty(\mathbb{R}^{3n},\mathbb{R})$, $\nabla V \in L^\infty(\mathbb{R}^{3n},\mathbb{R}^{3n})$. Then for all $i,k \in \{1,...,n\}$ and $j,l \in \{1,2,3\}$ and for any $\psi \in C_0^\infty(\mathbb{R}^{3n})$

(i) $[X_{i_j}, X_{k_l}] = 0$ on $C_0^\infty(\mathbb{R}^{3n})$, since

$$([X_{i_j}, X_{k_l}]\psi)(x) = x_{i_j}x_{k_l}\psi(x) - x_{k_l}x_{i_j}\psi(x) = 0.$$

(ii) $[P_{i_j}, P_{k_l}] = 0$ on $C_0^\infty(\mathbb{R}^{3n})$, since

$$([P_{i_j}, P_{k_l}]\psi)(x) = -\frac{\partial^2\psi}{\partial x_{i_j}\partial x_{k_l}}(x) + \frac{\partial^2\psi}{\partial x_{k_l}\partial x_{i_j}}(x) = 0$$

(using symmetry of second derivatives).

(iii) $[X_{i_j}, P_{k_l}] = i\delta_{i_jk_l}Id$ on $C_0^\infty(\mathbb{R}^{3n})$ (where δ is the well known Kronecker-delta), since

$$([X_{i_j}, P_{k_l}]\psi)(x) = -ix_{i_j}\frac{\partial\psi}{\partial x_{k_l}}(x) + i\frac{\partial(\psi x_{i_j})}{\partial x_{k_l}}(x) = i\delta_{i_jk_l}\psi(x).$$

(iv) $[H, X_{i_j}] = -iP_{i_j}$ on $C_0^\infty(\mathbb{R}^{3n})$, since

$$\begin{aligned}([H, X_{i_j}]\psi)(x) &= ([-\frac{1}{2}\triangle, X_{i_j}]\psi)(x) + ([V, X_{i_j}]\psi)(x)\\ &= -\frac{1}{2}\sum_{\alpha=1}^{n}\sum_{\beta=1}^{3}\left(\frac{\partial}{\partial x_{\alpha_\beta}}\left[\frac{\partial}{\partial x_{\alpha_\beta}}, X_{i_j}\right] + \left[\frac{\partial}{\partial x_{\alpha_\beta}}, X_{i_j}\right]\frac{\partial}{\partial x_{\alpha_\beta}}\right)\psi(x)\\ &= -\frac{1}{2}\sum_{\alpha=1}^{n}\sum_{\beta=1}^{3}(2\delta_{i_j\alpha_\beta})\frac{\partial\psi}{\partial x_{\alpha_\beta}}(x) = -\frac{\partial\psi}{\partial x_{i_j}}(x) = -iP_{i_j}\psi(x)\end{aligned}$$

using properties of the commutator stated in Lemma 1.6.3.

(v) $[H, P_{i_j}] = i(\frac{\partial V}{\partial x_{i_j}})$ on $C_0^\infty(\mathbb{R}^{3n})$, since

$$\begin{aligned}([H, P_{i_j}]\psi)(x) &= ([-\frac{1}{2}\triangle, P_{i_j}]\psi)(x) + ([V, P_{i_j}]\psi)(x)\\ &= ([V, P_{i_j}]\psi)(x) = i(\frac{\partial V}{\partial x_{i_j}})\psi(x)\end{aligned}$$

again using properties of the commutator stated in Lemma 1.6.3.

This section of introductory mathematical concepts is concluded with a basic problem from physics about the "domain problem":

Example 1.6.5
Let $H = -\frac{1}{2}\triangle + V$, $V : \mathbb{R}^3 \to \mathbb{R}$, $V(x) = -1/\|x\|_2$ be the Hamiltonian of the hydrogen atom and P be the momentum operator. The commutator $HP - PH$ is not defined on $C_0^\infty(\mathbb{R}^{3n})$, since $i[H, P] = [H, \nabla] = [-\frac{1}{2}\triangle, \nabla] + [V, \nabla] = -\nabla V(x) = -x/\|x\|_2^3$. But $-x/\|x\|_2^3$ does not map $C_0^\infty(\mathbb{R}^3)$ into $L^2(\mathbb{R}^3)$, because the singularity at zero behaves like $\|x\|_2^{-2}$ and hence $\|\nabla V\psi\|_{L^2}^2 = \int_{\mathbb{R}^3} |\nabla V(x)\psi(x)|^2 dx = \infty$ for all $\psi \in C_0^\infty(\mathbb{R}^3)$ with $\psi(0) \neq 0$. Hence, we found an operator whose domain is not dense in $L^2(\mathbb{R}^{3n})$.

2 Evolution of Angular Momentum Expectation

2.1 Ehrenfest's theorem and its abstract version

In quantum physics, a well known result asserts that the mean position and momentum of a quantum system in $\mathbb{R}^{3n}$ with Hamiltonian

$$H = -\sum_{i=1}^{n}\sum_{j=1}^{3}\frac{m_{i_j}}{2}\frac{\partial^2}{\partial x_{i_j}^2} + V$$

evolve "classically"

$$\frac{d}{dt}\langle X_{i_j}\rangle_{\psi(t)} = \frac{1}{m_{i_j}}\langle P_{i_j}\rangle_{\psi(t)} \tag{4}$$

and

$$\frac{d}{dt}\langle P_{i_j}\rangle_{\psi(t)} = \langle -\frac{\partial V}{\partial x_{i_j}}\rangle_{\psi(t)} \tag{5}$$

(Ehrenfest's equations, [Ehr27]). These are equations of Newtonian form for the time rate of change of the quantum mechanical mean values of position and momentum. The evolution of mean values as in (4), (5), besides being of interest in its own right, plays an important role in the study of quantum-classical coupling in molecular dynamics (see e.g. [BNS96]).

The heuristic justification, which can be found in any text book on quantum mechanics (see e.g. [GS03]), goes as follows. When H and A are symmetric, formally differentiating the mean value and substituting it into the Schrödinger equation (1) yields

$$\frac{d}{dt}\langle A\rangle_{\psi(t)} = i\langle [H,A]\rangle_{\psi(t)}. \tag{6}$$

When H is of the form (2) and A is a component of the position or momentum operator, formal evaluation of the commutator gives (4) and (5). While (6) and its derivation make mathematically sense when H and A are bounded, realistic quantum Hamiltonians and observables are unbounded and only defined on dense domains. Rigorous versions are not difficult to obtain in the context of classical, rapidly decaying solutions for smooth potentials [BEH94] or when A is relatively bounded with respect to H. For a rigorous treatment of operators A which are not relatively bounded and for an application to atomic and molecular systems with Coloumb interactions see [FK09], and for a sharper version for general self-adjoint operators, see [FS10].

One of the main results in [FK09] is Theorem 2.1.1 about the abstract Ehrenfest theorem. It is the basis for a rigorous derivation of the evolution of angular momentum expectations.

Theorem 2.1.1 (abstract Ehrenfest theorem)
Let H and A be two densely defined linear operators on a Hilbert space $\mathcal{H}$ such that

(H1) $H : D(H) \to \mathcal{H}$ is self-adjoint, $A : D(A) \to \mathcal{H}$ is symmetric.

(H2) e^{-itH} leaves $D(A) \cap D(H)$ invariant for all $t \in \mathbb{R}$.

(H3) For any $\psi_0 \in D(A) \cap D(H)$,

$$\sup_{t \in I} \|Ae^{-itH}\psi_0\|_{L^2} < \infty$$

for $I \subset \mathbb{R}$ bounded.

Then for $\psi_0 \in D(A) \cap D(H)$, the expected value $\langle A \rangle_{\psi(t)}$, $\psi(t) := e^{-itH}\psi_0$, is continuously differentiable with respect to t and satisfies

$$\frac{d}{dt}\langle A \rangle_{\psi(t)} = i\Big(\langle H\psi(t), A\psi(t)\rangle - \langle A\psi(t), H\psi(t)\rangle\Big). \tag{7}$$

Proof: See [FK09].

■

The right hand side in (7) allows to overcome the domain difficulties described in Example 1.6.5. This representation in (7) exploits the elementary but important observation that in equation (6), the commutator is not needed as an operator, but only as a quadratic form. When ψ belongs to the smaller set $D(AH) \cap D(HA)$, (7) reduces to the classical definition $\langle \psi, (HA - AH)\psi \rangle$.

2.2 Angular momentum operator

In this thesis, the abstract Ehrenfest theorem forms the basis for the derivation of an Ehrenfest equation for the angular momentum. To be able to apply the abstract Ehrenfest theorem, we have to define the angular momentum operator on a certain domain in such a way that the operator is well-defined and symmetric.

Definition 2.2.1 (angular momentum operator)
The *angular momentum operator* L is the cross product of the position and momentum operator, i.e. $L := X \wedge P$ on domain $D(L) \subset L^2(\mathbb{R}^{3n})$. The j^{th} component of the angular momentum operator of the i^{th} particle of a quantum system in $\mathbb{R}^{3n}$ is

$$L_{i_j} := \varepsilon_{j,\alpha,\beta} X_{i_\alpha} P_{i_\beta}, \quad (L_{i_j}\psi)(x) = \varepsilon_{j,\alpha,\beta} x_{i_\alpha} p_{i_\beta} \psi(x) \ \text{ on } \ D(L_{i_j}) \subset L^2(\mathbb{R}^{3n}), \tag{8}$$

using the Levi-Civita symbol and the Einstein notation.

□

For convenience – similar to the momentum operator – the focus is on components, rather than on the whole angular momentum operator L. Note that without loss of generality all proofs are done for the first component of the angular momentum operator of the i^{th} particle of a quantum system in $\mathbb{R}^{3n}$. Without this convention, the Levi-Civita symbol and the Einstein notation would cause needless case differentiations. So the reader's focus should be on

$$L_{i_1} = X_{i_2}P_{i_3} - X_{i_3}P_{i_2}, \quad (L_{i_1}\psi)(x) = (x_{i_2}p_{i_3} - x_{i_3}p_{i_2})\psi(x).$$

Up to now, it is not obvious on which domain $D(L_{i_j})$ the operator is well-defined, but the following lemma provides a satisfactory domain.

Lemma 2.2.2 (well-definedness of L_{i_j})
Let L_{i_j} be given by (8) and

$$D(L_{i_j}) := H^2(\mathbb{R}^{3n}) \cap \{\psi \in L^2(\mathbb{R}^{3n}) | \int_{\mathbb{R}^{3n}} |x_{i_k}^2 \psi(x)|^2 dx < \infty, k \in \{1,2,3\}\}. \tag{9}$$

Then L_{i_j} is a well-defined operator with a dense domain, i.e

$$L_{i_j} : D(L_{i_j}) \to L^2(\mathbb{R}^{3n}) \text{ and } C_0^\infty(\mathbb{R}^{3n}) \subset D(L_{i_j}) \subset L^2(\mathbb{R}^{3n}).$$

Proof: First we consider the denseness. Let $\psi \in C_0^\infty(\mathbb{R}^{3n})$ and choose a ball $B_R(0) \subset \mathbb{R}^{3n}$ containing the support of ψ. Then $\psi \in H^2(\mathbb{R}^{3n})$ and

$$\int_{\mathbb{R}^{3n}} |x_{i_k}^2 \psi(x)|^2 dx = \int_{B_R(0)} |x_{i_k}^2 \psi(x)|^2 dx \le \sup_{x \in B_R(0)} |x_{i_k}^4| \int_{B_R(0)} |\psi(x)|^2 dx \le R^4 \|\psi\|_{L^2}^2.$$

Hence, $C_0^\infty(\mathbb{R}^{3n}) \subset D(L_{i_1})$ and the domain is dense in $L^2(\mathbb{R}^{3n})$. For well-definedness let $\psi \in D(L_{i_1})$, then (using integration by parts and the notation $\partial_{i_j} := \frac{\partial}{\partial x_{i_j}}$)

$$\begin{aligned}
\|L_{i_1}\psi\|_{L^2}^2 &= \int_{\mathbb{R}^{3n}} |(x_{i_2}p_{i_3} - x_{i_3}p_{i_2})\psi(x)|^2 dx \\
&= \int_{\mathbb{R}^{3n}} \overline{(x_{i_2}\partial_{i_3} - x_{i_3}\partial_{i_2})\psi(x)} (x_{i_2}\partial_{i_3} - x_{i_3}\partial_{i_2})\psi(x) dx \\
&= \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_2} \overline{(\partial_{i_3}\psi)(x)} (\partial_{i_3}\psi)(x) dx + \int_{\mathbb{R}^{3n}} x_{i_3}x_{i_3} \overline{(\partial_{i_2}\psi)(x)} (\partial_{i_2}\psi)(x) dx \\
&\quad - \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_3} \overline{(\partial_{i_3}\psi)(x)} (\partial_{i_2}\psi)(x) dx - \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_3} \overline{(\partial_{i_2}\psi)(x)} (\partial_{i_3}\psi)(x) dx \\
&= - \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_2} \overline{\psi(x)} (\partial_{i_3}^2\psi)(x) dx - \int_{\mathbb{R}^{3n}} x_{i_3}x_{i_3} \overline{\psi(x)} (\partial_{i_2}^2\psi)(x) dx \\
&\quad + \int_{\mathbb{R}^{3n}} x_{i_3} \overline{(\partial_{i_3}\psi)(x)} \psi(x) dx + \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_3} \overline{(\partial_{i_2}\partial_{i_3}\psi)(x)} \psi(x) dx \\
&\quad + \int_{\mathbb{R}^{3n}} x_{i_2} \overline{(\partial_{i_2}\psi)(x)} \psi(x) dx + \int_{\mathbb{R}^{3n}} x_{i_2}x_{i_3} \overline{(\partial_{i_3}\partial_{i_2}\psi)(x)} \psi(x) dx.
\end{aligned}$$

The symmetry of second derivatives and the Cauchy Schwartz inequality lead to

$$\begin{aligned} \|L_{i_1}\psi\|_{L^2}^2 \leq \|x_{i_2}^2\psi\|_{L^2}\|\partial_{i_3}^2\psi\|_{L^2} + \|x_{i_3}^2\psi\|_{L^2}\|\partial_{i_2}^2\psi\|_{L^2} \\ + \|x_{i_3}\psi\|_{L^2}\|\partial_{i_3}\psi\|_{L^2} + \|x_{i_2}\psi\|_{L^2}\|\partial_{i_2}\psi\|_{L^2} \\ + 2\|x_{i_2}x_{i_3}\psi\|_{L^2}\|\partial_{i_2}\partial_{i_3}\psi\|_{L^2}. \end{aligned} \tag{10}$$

Finally with the Young inequality ($ab \leq \frac{a^2}{2} + \frac{b^2}{2}$ for $a, b \in \mathbb{R}^+$) we obtain

$$\begin{aligned} \|x_{i_2}x_{i_3}\psi\|_{L^2}^2 &= \left(\int_{\mathbb{R}^{3n}} x_{i_2}^2 x_{i_3}^2 |\psi(x)|^2 dx\right) \leq \left(\int_{\mathbb{R}^{3n}} \left(\frac{x_{i_2}^4}{2} + \frac{x_{i_3}^4}{2}\right)|\psi(x)|^2 dx\right) \\ &= \frac{1}{2}\left(\|x_{i_2}^2\psi\|_{L^2}^2 + \|x_{i_3}^2\psi\|_{L^2}^2\right) \end{aligned}$$

and

$$\|x_{i_j}\psi\|_{L^2}^2 \leq \frac{1}{2}\left(\|x_{i_j}^2\psi\|_{L^2}^2 + \|\psi\|_{L^2}^2\right), \ \ j \in \{2, 3\}.$$

Since $\psi \in D(L_{i_1})$, all norms are finite and this establishes the assertion.

■

Lemma 2.2.3 (symmetry of L_{i_j} on $D(L_{i_j})$)
Let L_{i_j} be given by (8) and (9). Then L_{i_j} is symmetric.

Proof: Let ψ, $\phi \in D(L_{i_1})$, then (using integration by parts)

$$\begin{aligned} \langle L_{i_1}\psi, \phi\rangle &= \int_{\mathbb{R}^{3n}} \overline{(x_{i_2}p_{i_3} - x_{i_3}p_{i_2})\psi(x)}\phi(x)dx \\ &= \int_{\mathbb{R}^{3n}} x_{i_2}\overline{(p_{i_3}\psi)(x)}\phi(x)dx - \int_{\mathbb{R}^{3n}} x_{i_3}\overline{(p_{i_2}\psi)(x)}\phi(x)dx \\ &= \int_{\mathbb{R}^{3n}} x_{i_2}\overline{\psi(x)}(p_{i_3}\phi)(x)dx - \int_{\mathbb{R}^{3n}} x_{i_3}\overline{\psi(x)}(p_{i_2}\phi)(x)dx \\ &= \langle\psi, L_{i_1}\phi\rangle. \end{aligned}$$

The inequalities of Cauchy Schwartz and Young yield convergence of all integrals (c.f. proof of Lemma 2.2.2); hence, L_{i_1} is symmetric.

■

2.3 Evolution of expected angular momentum

The goal in this thesis is to derive the evolution of angular momentum expectation in the following situation:

$$H = -\frac{1}{2}\triangle + V, \quad \mathcal{H} = L^2(\mathbb{R}^{3n}), \quad D(H) = H^2(\mathbb{R}^{3n}) \tag{11}$$

with

$$V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R}) \qquad \text{and} \qquad \nabla V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R}^{3n}). \tag{12}$$

The main result of this thesis is the following Theorem 2.3.1. The result in b) is to the best of my knowledge, so far missing from the literature.

Theorem 2.3.1 (evolution of expected angular momentum)
Let H be a Hamiltonian of form (2) satisfying (11) and (12). Let L_{i_j} be the j^{th} component of the angular momentum operator of the i^{th} particle of a quantum system in $\mathbb{R}^{3n}$ (see (8), (9)). Abbreviate $\psi(t) := e^{-itH}\psi_0$, then

a) e^{-itH} leaves $D(L_{i_j}) \cap D(H)$ invariant for all $t \in \mathbb{R}$.

b) $\langle L_{i_j}\rangle_{\psi(t)}$ is continuously differentiable with respect to t for any $\psi_0 \in D(L_{i_j}) \cap D(H)$ and satisfies
$$\frac{d}{dt}\langle L_{i_j}\rangle_{\psi(t)} = \langle -(X_{i\bullet} \wedge \nabla_i V)_j\rangle_{\psi(t)}, \tag{13}$$

where $X_{i\bullet}$ is the position operator of the i^{th} particle and $\nabla_i V$ is the partial derivative of V in the $x_{i\bullet}$ direction.

The invariance in a) amounts to the, far from obvious, assertion that finiteness of the fourth moment of the probability distribution of position, $\int_{\mathbb{R}^{3n}} |x|^4 |\psi(x,t)|^2 dx$, is preserved by the Schrödinger evolution (called "dynamics") for bounded potentials. For higher moments, or even for monomials $M(x_1, ..., x_l)$ of degree n in the coordinates, [HU66] provides interesting results in terms of preservation of finiteness of integrals $\int_{\mathbb{R}^{3n}} |M(x_1, ...x_l)|^2 |\psi(x,t)|^2 dx$ by the dynamics.

The requirement that $V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R})$ guarantees that H is self-adjoint with domain $H^2(\mathbb{R}^{3n})$, and hence generates a unique strongly continuous unitary group $e^{-itH}, t \in \mathbb{R}$ (see Corollary 1.5.3 and Corollary 1.4.3). The requirement that $\nabla V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R}^{3n})$ is related to the appearance of ∇V in (13).

Similar to the heuristic justification of Ehrenfest equations (4) and (5), formal evaluation of the commutator $[H, L_{i_j}]$ and substituting in equation (6) gives (13). But a mathematically rigorous derivation leads directly to the following issues, some of which have been pointed out in the physics literature, see e.g. [Hil73].

(1) First, the expected value $\langle \psi(t), L_{i_j}\psi(t)\rangle$ is only well-defined provided $\psi(t)$ belongs to the domain $D(L_{i_j})$, as pointed out in Definition 1.6.1. But it is not clear that $D(L_{i_j})$ is invariant under the dynamics.

(2) Second, even if $\psi(t)$ stays in the domain $D(L_{i_j})$, it needs to be shown that $\langle L_{i_j}\rangle_{\psi(t)}$ is differentiable in time. A priori, it does not seem obvious that this expression is even continuous.

3 Proof of Theorem 2.3.1

The proof of Theorem 2.3.1 relies on the verification of (H1), (H2) and (H3) of the abstract Ehrenfest theorem. (H1) is already verified by Corollary 1.5.3 and Lemma 2.2.3. Hence, the focus is on proving (H2) and (H3). Important for proving Theorem 2.3.1 is a derivation of bounds for $\|L_{i_j}\psi(t)\|_{L^2}$, which is done in the next lemma. For convenience, we note all constants with the same letter C, except of the constant C_V which is introduced in Example 1.2.3(i). The reason is that as long as the constants are finite and independent of t, we are not interested in the specific value of them.

Lemma 3.1
Let H be a Hamiltonian of form (2) satisfying (11) and (12) and L_{i_j} be given by (8), (9). Let $\psi_0 \in D(H) \cap D(L_{i_j})$ and abbreviate $\psi(t) := e^{-itH}\psi_0$, then

$$\|L_{i_j}\psi(t)\|_{L^2}^2 \leq CM(1+|t|)^2 \sup A \tag{14}$$

with a constant C independent of t, $M := \big(\|H\psi_0\|_{L^2} + \|\psi_0\|_{L^2}\big)$ and the set

$$A := \Big\{ \|\psi_0\|_{L^2}, \|x_{i_k}\psi_0\|_{L^2}, \|x_{i_k}^2\psi_0\|_{L^2}, \|H\psi_0\|_{L^2} \mid k \in \{1,2,3\}\backslash\{j\} \Big\}.$$

Proof: The idea of the proof is to use inequality (10) for $\psi(t)$; all steps to obtain inequality (10) (the Cauchy Schwartz inequality, symmetry of second derivatives and integration by parts) are applicable to the here stated situation, since $\psi(t) \in H^2(\mathbb{R}^{3n})$ by Lemma 1.4.5(ii).

$$\begin{aligned}
\|L_{i_1}\psi(t)\|_{L^2}^2 \leq\ & \underbrace{\|x_{i_2}^2\psi(t)\|_{L^2}}_{****}\underbrace{\|\partial_{i_3}^2\psi(t)\|_{L^2}}_{*} + \underbrace{\|x_{i_3}^2\psi(t)\|_{L^2}}_{****}\underbrace{\|\partial_{i_2}^2\psi(t)\|_{L^2}}_{*} \\
& + \underbrace{\|x_{i_3}\psi(t)\|_{L^2}}_{***}\underbrace{\|\partial_{i_3}\psi(t)\|_{L^2}}_{*} + \underbrace{\|x_{i_2}\psi(t)\|_{L^2}}_{***}\underbrace{\|\partial_{i_2}\psi(t)\|_{L^2}}_{*} \\
& + 2\underbrace{\|x_{i_2}x_{i_3}\psi(t)\|_{L^2}}_{**}\underbrace{\|\partial_{i_2}\partial_{i_3}\psi(t)\|_{L^2}}_{*}.
\end{aligned}$$

ad ($*$): Due to the fact that $\psi(t) \in H^2(\mathbb{R}^{3n})$, all norms are finite for fixed $t \in \mathbb{R}$. It is possible to bound these differential operators relatively to the Hamiltonian using Plancherel's theorem and the fact that V is a bounded operator (see Example 1.2.3(i)). To show the relatively boundedness, note that $\sqrt{a^2+b^2} \leq a+b$ for any $a, b \in R^+$; let $i, \tau \in \{1, ..., n\}$, $j, l \in \{1,2,3\}$, then

$$\begin{aligned}
\|\partial_{i_j}\psi(t)\|_{L^2} &= \|\widehat{\partial_{i_j}\psi(t)}\|_{L^2} = \|k_{i_j}\hat{\psi}(t)\|_{L^2} \overset{\text{Young}}{\leq} \Big(\frac{1}{2}\big(\|k_{i_j}^2\hat{\psi}(t)\|_{L^2}^2 + \|\hat{\psi}(t)\|_{L^2}^2\big)\Big)^{\frac{1}{2}} \\
&\leq \Big(\frac{1}{2}\big(\|\sum_{\alpha=1}^{n}\sum_{\beta=1}^{3} k_{\alpha_\beta}^2\hat{\psi}(t)\|_{L^2}^2 + \|\hat{\psi}(t)\|_{L^2}^2\big)\Big)^{\frac{1}{2}} = \Big(\frac{1}{2}\big(\|\triangle\psi(t)\|_{L^2}^2 + \|\psi(t)\|_{L^2}^2\big)\Big)^{\frac{1}{2}} \\
&\leq C\big(\|\triangle\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \leq C\big(\| -\frac{1}{2}\triangle\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \\
&= C\big(\|(H-V)\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \leq C\big(\|H\psi(t)\|_{L^2} + \|V\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \\
&\leq C\big(\|H\psi(t)\|_{L^2} + C_V\|\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \leq C\big(\|H\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) \\
&= C\big(\|H\psi_0\|_{L^2} + \|\psi_0\|_{L^2}\big)
\end{aligned}$$

by the conservation of quantities (Corollary 1.4.5(iii)). The bound for the partial derivatives of second order is left:

$$\begin{aligned}
\|\partial_{i_j}\partial_{\tau_l}\psi(t)\|_{L^2} &= \|\partial_{i_j}\widehat{\partial_{\tau_l}\psi}(t)\|_{L^2} = \|k_{i_j}k_{\tau_l}\hat{\psi}(t)\|_{L^2} \overset{\text{Young}}{\leq} \Big(\frac{1}{2}\big(\|k_{i_j}^2\hat{\psi}(t)\|_{L^2}^2 + \|k_{\tau_l}^2\hat{\psi}(t)\|_{L^2}^2\big)\Big)^{\frac{1}{2}} \\
&\leq \|\sum_{\alpha=1}^{n}\sum_{\beta=1}^{3} k_{\alpha_\beta}^2\hat{\psi}(t)\|_{L^2} = \|\triangle\psi(t)\|_{L^2} \leq C\| -\frac{1}{2}\triangle\psi(t)\|_{L^2} \\
&\leq C\big(\|H\psi(t)\|_{L^2} + \|V\psi(t)\|_{L^2}\big) \leq C\big(\|H\psi(t)\|_{L^2} + C_V\|\psi(t)\|_{L^2}\big) \\
&\leq C\big(\|H\psi(t)\|_{L^2} + \|\psi(t)\|_{L^2}\big) = C\big(\|H\psi_0\|_{L^2} + \|\psi_0\|_{L^2}\big).
\end{aligned}$$

ad $(**)$: The Young inequality yields

$$\|x_{i_2}x_{i_3}\psi(t)\|_{L^2} \leq \Big(\frac{1}{2}\big(\|x_{i_2}^2\psi(t)\|_{L^2}^2 + \|x_{i_3}^2\psi(t)\|_{L^2}^2\big)\Big)^{\frac{1}{2}} \leq C\big(\|x_{i_2}^2\psi(t)\|_{L^2} + \|x_{i_3}^2\psi(t)\|_{L^2}\big).$$

These are norms examined in $(****)$.

ad $(***)$: Thanks to [HU66], these norms are easy to handle. As a result, we can assume that finiteness of the second moment of the probability distribution of position is preserved under dynamics, i.e. for any $\psi_0 \in D(H) \cap D(X_{i_j})$

$$\|x_{i_j}\psi(t)\|_{L^2} \leq C\big(1+|t|\big)\sup\Big\{\|\psi_0\|_{L^2}, \|x_{i_j}\psi_0\|_{L^2}, \|H\psi_0\|_{L^2}\Big\}. \tag{15}$$

For definition of $D(X_{i_j})$, see Example 1.2.3(iii). By the Young inequality, it is easy to show that $\big(D(L_{i_j}) \cap D(H)\big) \subset \big(D(X_{i_j}) \cap D(H)\big)$. Thus, the inequality (15) is applicable to the situation stated in this lemma.

ad $(****)$: Again we use [HU66]. We can assume that for any $\psi_0 \in D(X_{i_j}^2) \cap D(H)$

$$\|x_{i_j}^2 \psi(t)\|_{L^2} \leq C\big(1+|t|\big)^2 \sup\Big\{\|\psi_0\|_{L^2}, \|x_{i_j}\psi_0\|_{L^2}, \|x_{i_j}^2\psi_0\|_{L^2}, \|H\psi_0\|_{L^2}\Big\}, \tag{16}$$

where

$$D(X_{i_j}^2) := \{\psi \in L^2(\mathbb{R}^{3n}) \mid \int_{\mathbb{R}^{3n}} |x_{i_j}^2 \psi(x)|^2 dx < \infty\}.$$

Hence, $\big(D(L_{i_j}) \cap D(H)\big) \subset \big(D(X_{i_j}^2) \cap D(H)\big)$ and the inequality (16) is applicable.

Additionally, $(1+|t|) \leq (1+|t|)^2$ for any $t \in \mathbb{R}$. The analysis of all norms yields the assertion.

■

The bound (14) given by Lemma 3.1 is already sufficient for applying the abstract Ehrenfest theorem on H and L_{i_j}.

Proposition 3.2
Let H be a Hamiltonian of form (2) satisfying (11) and (12) and L_{i_j} be given by (8), (9). Let $\psi_0 \in D(H) \cap D(L_{i_j})$ and abbreviate $\psi(t) := e^{-itH}\psi_0$. Then:
$\langle L_{i_j}\rangle_{\psi(t)}$ is continuously differentiable with respect to t for any $\psi_0 \in D(L_{i_j}) \cap D(H)$ and satisfies

$$\frac{d}{dt}\langle L_{i_j}\rangle_{\psi(t)} = i\Big(\langle H\psi(t), L_{i_j}\psi(t)\rangle - \langle L_{i_j}\psi(t), H\psi(t)\rangle\Big). \tag{17}$$

Proof: So far, the entire analysis was done to apply the abstract Ehrenfest theorem to the situation stated in this proposition. (H1) is already verified by Corollary 1.5.3 and Lemma 2.2.3.

(H2): By Corollary 1.4.5(ii), e^{-itH} leaves $D(H)$ invariant for all $t \in \mathbb{R}$. Hence, there is only left to prove that $\|x_{i_j}^2\psi(t)\|_{L^2}$ is finite for any $\psi_0 \in D(L_{i_j}) \cap D(H)$ and all $t \in \mathbb{R}$. Using inequality (16), we have to show that the norms $\|\psi_0\|_{L^2}, \|x_{i_j}\psi_0\|_{L^2}, \|x_{i_j}^2\psi_0\|_{L^2}$ and $\|H\psi_0\|_{L^2}$ are finite. But this follows from $\psi_0 \in D(L_{i_j}) \cap D(H)$ and the fact that the Young inequality yields $\|x_{i_j}\psi_0\|_{L^2} \leq C\big(\|x_{i_j}^2\psi_0\|_{L^2} + \|\psi_0\|_{L^2}\big)$.

(H3): Applying bound (14), it follows that $\|L_{i_j}\psi(t)\|_{L^2}$ stays bounded for t in a bounded set $I \subset \mathbb{R}$.

The assertion follows from the abstract Ehrenfest theorem. Additionally, the considerations for proving (H2) lead to a proof for Theorem 2.3.1 a).

■

Note, however, that so far the Ehrenfest equation for angular momentum is not fully derived, since it remains to be verified that the right hand side in (17) agrees with the right hand side in (13). For this, the additional assumption $\nabla V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R}^{3n})$ is needed.

Proof of Theorem 2.3.1. b):
To complete the proof of the statements, we need to show that

$$i\Big(\langle H\psi, L_{i_1}\psi\rangle - \langle L_{i_1}\psi, H\psi\rangle\Big) = \langle -(X_{i\bullet} \wedge \nabla_i V)_1\rangle_\psi \tag{18}$$

for all $\psi \in H^2(\mathbb{R}^{3n}) \cap D(L_{i_1})$.

first step: For functions $\psi \in C_0^\infty(\mathbb{R}^{3n})$, this follows from an elementary calculation. We know by Corollary 1.5.3 and Lemma 2.2.3 that H and L_{i_j} are symmetric on $C_0^\infty(\mathbb{R}^{3n})$, and hence

$$\begin{aligned} i\Big(\langle H\psi, L_{i_1}\psi\rangle - \langle L_{i_1}\psi, H\psi\rangle\Big) &= i\Big(\langle \psi, HL_{i_1}\psi\rangle - \langle \psi, L_{i_1}H\psi\rangle\Big) \\ &= i\Big(\langle \psi, \big(HL_{i_1} - L_{i_1}H\big)\psi\rangle\Big) \\ &= i\Big(\langle \psi, [H, L_{i_1}]\psi\rangle\Big). \end{aligned} \tag{19}$$

Using again the Cauchy Schwartz inequality, it is straightforward to show that the inner products in (19) converge for all $\psi \in C_0^\infty(\mathbb{R}^{3n})$ and hence calculation (19) is correct. Further, the calculation of $[H, L_{i_1}]$ on $C_0^\infty(\mathbb{R}^{3n})$ is needed. But Example 1.6.4 leads to

$$\begin{aligned} [H, L_{i_1}] &= [H, X_{i_2}P_{i_3}] - [H, X_{i_3}P_{i_2}] \\ &= [H, X_{i_2}]P_{i_3} + X_{i_2}[H, P_{i_3}] - [H, X_{i_3}]P_{i_2} - X_{i_3}[H, P_{i_2}] \\ &= -iP_{i_2}P_{i_3} + iX_{i_2}(\partial_{i_3}V) + iP_{i_3}P_{i_2} - iX_{i_3}(\partial_{i_2}V) \\ &= i(X_{i\bullet} \wedge \nabla_i V)_1, \end{aligned} \tag{20}$$

using commutator properties stated in Lemma 1.6.3 and the symmetry of second derivatives. Hence (19) and (20) establish (18) for functions in $C_0^\infty(\mathbb{R}^{3n})$.

second step: Simplifying equation (18), one obtains

$$i\Big(\langle H\psi, X_{i_2}P_{i_3}\psi\rangle - \langle H\psi, X_{i_3}P_{i_2}\psi\rangle - \langle X_{i_2}P_{i_3}\psi, H\psi\rangle + \langle X_{i_3}P_{i_2}\psi, H\psi\rangle\Big)$$

$$\stackrel{!}{=} -\langle \psi, X_{i_2}(\partial_{i_3}V)\psi\rangle + \langle \psi, X_{i_3}(\partial_{i_2}V)\psi\rangle \text{ for all } \psi \in H^2(\mathbb{R}^{3n}) \cap D(L_{i_1}).$$

Now consider functions $\psi \in H^2(\mathbb{R}^{3n})$ with compact support. Clearly, it suffices to approximate ψ by a sequence ψ_ε of $C_0^\infty(\mathbb{R}^{3n})$ functions in such a way that the six terms appearing inside the inner products,

$$H\psi_\varepsilon, \qquad X_{i_2}P_{i_3}\psi_\varepsilon, \qquad X_{i_3}P_{i_2}\psi_\varepsilon, \qquad X_{i_2}(\partial_{i_3}V)\psi_\varepsilon, \qquad X_{i_3}(\partial_{i_2}V)\psi_\varepsilon, \qquad \psi_\varepsilon,$$

converge in L^2 to the corresponding terms for ψ. Therefore, choose a ball $B_R(0)$ containing the support of ψ. Consider the following standard approximation obtained by mollification:

$$\psi_\varepsilon(x) := (\eta_\varepsilon * \psi)(x) = \int_{\mathbb{R}^{3n}} \eta_\varepsilon(x-y)\psi(y)\mathrm{dy},$$

where $\eta_\varepsilon(x) = \varepsilon^{-3n}\eta(x\backslash\varepsilon)$, $\varepsilon \in (0,1)$, $\eta \in C_0^\infty(\mathbb{R}^{3n})$, $\eta = 0$ outside $B_1(0)$; then (see e.g. [Eva10a]) $\psi_\varepsilon \in C_0^\infty(\mathbb{R}^{3n})$, $\mathrm{supp}(\psi), \mathrm{supp}(\psi_\varepsilon) \subset B_{R+1}(0)$ and $\psi_\varepsilon \to \psi$ in H^2.

It is easy to check that the identity Id and P_{i_j} are continuous operators from $H^2(\mathbb{R}^{3n})$ to $L^2(\mathbb{R}^{3n})$ (to show this, use the H^2 norm defined in Example 1.2.3(ii)); hence, $\psi_\varepsilon \to \psi$ in L^2 and $P_{i_j}\psi_\varepsilon \to P_{i_j}\psi$ in L^2. Moreover, H is a continuous operator from $H^2(\mathbb{R}^{3n})$ to $L^2(\mathbb{R}^{3n})$, since

$$\begin{aligned}\|H\psi\|_{L^2} &= \|(-\frac{1}{2}\triangle + V)\psi\|_{L^2} \le \| -\frac{1}{2}\triangle\psi\|_{L^2} + \|V\psi\|_{L^2} \\ &\le C\|\psi\|_{H^2} + C_V\|\psi\|_{L^2} \le C\|\psi\|_{H^2},\end{aligned}$$

so that $H\psi_\varepsilon \to H\psi$ in L^2.

Further, X_{i_j} is continuous on the subspace of $L^2(\mathbb{R}^{3n})$ functions with support in $B_{R+1}(0)$, since

$$\|X_{i_j}\psi\|_{L^2} = \|X_{i_j}\psi\|_{L^2(B_{R+1}(0))} \le \mathrm{sup}_{x\in B_{R+1}(0)}|x_{i_j}|\|\psi\|_{L^2} = (R+1)\|\psi\|_{L^2}.$$

In addition, $\psi_\varepsilon \in H^2(\mathbb{R}^{3n})$, $\mathrm{supp}(\psi_\varepsilon) \subset B_{R+1}(0)$ and so $P_{i_j}\psi_\varepsilon \in H^1(\mathbb{R}^{3n}) \subset L^2(\mathbb{R}^{3n})$ with $\mathrm{supp}(P_{i_j}\psi_\varepsilon) \subset B_{R+1}(0)$. Hence, $X_{i_2}P_{i_3}\psi_\varepsilon \to X_{i_2}P_{i_3}\psi$ in L^2 and $X_{i_3}P_{i_2}\psi_\varepsilon \to X_{i_3}P_{i_2}\psi$ in L^2, using continuity of P_{i_j} as a map from $H^2(\mathbb{R}^{3n})$ to $L^2(\mathbb{R}^{3n})$.

And finally we need the assumption that $\nabla V \in L^\infty(\mathbb{R}^{3n}, \mathbb{R}^{3n})$. It follows that $(\partial_{i_j}V)\psi_\varepsilon$ is a $L^2(\mathbb{R}^{3n})$ function with support in $B_{R+1}(0)$. Again, X_{i_j} is continuous on the subspace of $L^2(\mathbb{R}^{3n})$ functions with support in $B_{R+1}(0)$. As a result, $X_{i_3}(\partial_{i_2}V)\psi_\varepsilon \to X_{i_3}(\partial_{i_2}V)\psi$ and $X_{i_2}(\partial_{i_3}V)\psi_\varepsilon \to X_{i_2}(\partial_{i_3}V)\psi$ in L^2 by continuity of ∇V.

Thus we have proved that the six terms appearing inside the inner products (dependent on ψ_ε) converge in L^2 to the corresponding terms for ψ. This establishes (18) for compactly supported $H^2(\mathbb{R}^{3n})$ functions.

third step: Finally let ψ be a general function in $D(H) \cap D(L_{i_j})$. Let $\eta \in C_0^\infty(\mathbb{R}^{3n})$ with $\eta(0) = 1$. Then $\psi_R(x) := \eta(x \backslash R)\psi(x)$ is a compactly supported $H^2(\mathbb{R}^{3n})$ function, so (18) holds for ψ_R by the previous step. Further, it is straightforward to check that $\psi_R \to \psi$ in H^2. Similar to the considerations in the second step, we have to show that the six terms appearing inside the inner products

$$H\psi_R, \qquad X_{i_2}P_{i_3}\psi_R, \qquad X_{i_3}P_{i_2}\psi_R, \qquad X_{i_2}(\partial_{i_3}V)\psi_R, \qquad X_{i_3}(\partial_{i_2}V)\psi_R, \qquad \psi_R,$$

converge in L^2 to the corresponding terms for ψ. Here, it is trivial that $\psi_R \to \psi$ in L^2, since $\psi_R \to \psi$ in H^2.

$$\begin{aligned}\|H(\psi_R - \psi)\|_{L^2} &\leq \|\triangle(\psi_R - \psi)\|_{L^2} + \|V(\psi_R - \psi)\|_{L^2} \\ &\leq \|\psi_R - \psi\|_{H^2} + \|V\|_{L^\infty}\|\psi_R - \psi\|_{L^2},\end{aligned}$$

and hence $H\psi_R \to H\psi$ in L^2. Further let $k, l \in \{1, 2, 3\}$ with $k \neq l$, then

$$\begin{aligned}\|X_{i_k}P_{i_l}(\psi_R - \psi)\|_{L^2}^2 &= \int_{\mathbb{R}^{3n}} |x_{i_k}\partial_{i_l}\psi_R(x) - x_{i_k}\partial_{i_l}\psi(x)|^2 dx \\ &= \int_{\mathbb{R}^{3n}} x_{i_k}^2 \psi_R(x)\big(\overline{(\partial_{i_l}^2\psi)(x)} - \overline{(\partial_{i_l}^2\psi_R)(x)}\big)dx \\ &\quad + \int_{\mathbb{R}^{3n}} x_{i_k}^2 \psi(x)\big(\overline{(\partial_{i_l}^2\psi_R)(x)} - \overline{(\partial_{i_l}^2\psi)(x)}\big)dx\end{aligned}$$

by integration by parts. With the Cauchy Schwartz inequality we obtain

$$\begin{aligned}\|X_{i_k}P_{i_l}(\psi_R - \psi)\|_{L^2}^2 &\leq \|X_{i_k}^2\psi_R\|_{L^2}\|\partial_{i_l}^2(\psi - \psi_R)\|_{L^2} + \|X_{i_k}^2\psi\|_{L^2}\|\partial_{i_l}^2(\psi_R - \psi)\|_{L^2} \\ &\leq \|X_{i_k}^2\psi_R\|_{L^2}\|(\psi - \psi_R)\|_{H^2} + \|X_{i_k}^2\psi\|_{L^2}\|(\psi_R - \psi)\|_{H^2}.\end{aligned}$$

It can be shown that $X_{i_k}^2\psi$, $X_{i_k}^2\psi_R \in L^2(\mathbb{R}^{3n})$ by elementary calculations. As a consequence, $X_{i_k}P_{i_l}\psi_R$ converges to $X_{i_k}P_{i_l}\psi$ in L^2. And finally

$$\begin{aligned}\|X_{i_k}\big(\partial_{i_l}V\big)(\psi_R - \psi)\|_{L^2}^2 &\leq \|\nabla V\|_{L^\infty}^2\|X_{i_k}(\psi_R - \psi)\|_{L^2}^2 \\ &\leq \|\nabla V\|_{L^\infty}^2\big(\|X_{i_k}^2\psi_R\|_{L^2}\|\psi_R - \psi\|_{L^2} + \|X_{i_k}^2\psi\|_{L^2}\|\psi - \psi_R\|_{L^2}\big)\end{aligned}$$

again by integration by parts and the Cauchy Schwartz inequality. Hence,

$$X_{i_k}(\partial_{i_l}V)\psi_R \to X_{i_k}(\partial_{i_l}V)\psi \text{ in } L^2.$$

Consequently all the six terms appearing inside the inner products converge in L^2 to the corresponding terms for ψ, establishing (18) in the general case.

■

4 Interpretation

The motivation for the derivation of an Ehrenfest theorem for the angular momentum expectation was given by the equations

$$\frac{d}{dt}\langle X_{i_j}\rangle_{\psi(t)} = \frac{1}{m_{i_j}}\langle P_{i_j}\rangle_{\psi(t)} \qquad \text{and} \qquad \frac{d}{dt}\langle P_{i_j}\rangle_{\psi(t)} = \langle -\frac{\partial V}{\partial x_{i_j}}\rangle_{\psi(t)},$$

which are of Newtonian form. In other words, the mean values of position and momentum operator correspond to Newton's second law of motion $F = ma$,

$$\langle -\frac{\partial V}{\partial x_{i_j}}\rangle_{\psi(t)} = m_{i_j}\frac{d^2}{dt^2}\langle X_{i_j}\rangle_{\psi(t)}.$$

Here, F is the net force applied, m and a are the mass and acceleration of the body. Since in classical mechanics the time derivative of angular momentum is given by

$$\frac{d}{dt}(q \wedge p) = q \wedge \dot{p} = q \wedge F,$$

(where $q \wedge F$ is defined as the torque) in fact we derived the quantum mechanical analogy

$$\frac{d}{dt}\langle L_{i_j}\rangle_{\psi(t)} = \langle -(X_{i\bullet} \wedge \nabla_i V)_j\rangle_{\psi(t)}$$

under boundedness assumptions on V and ∇V. Consequently, the time evolution of angular momentum expectation equals the expected quantum mechanical torque.

Prototypical Hamiltonians satisfying these boundedness assumptions on V and ∇V are the Hamiltonians with potential wells of form

$$V(x) = \sum_{i=1}^{n} \min\{\|x_{i\bullet}\|_2^2, c_i\}, \qquad c_i \in \mathbb{R}, \quad x_{i\bullet} \in \mathbb{R}^3,$$

and for the smooth case

$$V(x) = \frac{\|x\|_2^2}{\|x\|_2^2 + c}\ , \qquad c \in \mathbb{R}^+.$$

Though, boundedness of V and ∇V is a strong assumption and does not include a variety of important potentials. A prospective goal could be to modify the assumptions to include atomic and molecular Hamiltonians with Coulomb interactions, e.g. the electronic Hamiltonian of a general molecule

$$H_{el} = -\frac{1}{2}\triangle + \sum_{i=1}^{n} v(x_{i\bullet}) + \sum_{1\leq i<j\leq n} \frac{1}{\|x_{i\bullet} - x_{j\bullet}\|_2}, \qquad v(x_{i\bullet}) = -\sum_{\alpha=1}^{m} \frac{Z_\alpha}{\|x_{i\bullet} - R_\alpha\|_2},$$

where $Z_\alpha > 0$ and $R_\alpha \in \mathbb{R}^3$ are the charges and coordinates of the nuclei. Atomic units have been used so that $\hbar = 1$ and the electrons have mass 1 and charge -1.

At the end of this thesis, we show that the time rate of change of angular momentum expectation vanishes, when assuming the potential V to be rotationally symmetric.

Corollary 4.1
Let H be a Hamiltonian of form (2) satisfying (11), (12) with a rotationally symmetric potential V. Further let L_{i_j} be given by (8), (9). Then

$$\frac{d}{dt}\langle L_{i_j}\rangle_{\psi(t)} = 0.$$

Proof: We can apply Theorem 2.3.1b) to the here stated situation. Since V is a rotationally symmetric potential, we may assume $V = u(r)$ with $r(x) := \|x\|_2$ and $u : \mathbb{R} \to \mathbb{R}$. Hence,

$$\nabla_i V(x) = \frac{x_{i\bullet}}{r(x)} u'(r(x)) \in \mathbb{R}^3$$

and

$$X_{i\bullet} \wedge \nabla_i V = \frac{u'(r)}{r}\big(X_{i\bullet} \wedge X_{i\bullet}\big) = 0.$$

■

When the time rate of change of observable's expectation equals zero, we name the observable a *quantum mechanical conserved quantity.* Motivated by Ehrenfest's equation for a general quantum mechanical operator,

$$\frac{d}{dt}\langle A\rangle_{\psi(t)} = i\langle [H, A]\rangle_{\psi(t)},$$

we say that those conserved quantities *commute with the Hamiltonian H.* For further discussions on quantum mechanical conserved quantities, see [Sch02].

References

[BEH94] J. Blank, P.Exner and M. Havliček. *Hilbert space operators in quantum physics.* Springer, New York, 1994.

[BNS96] F. Bornemann, P. Nettesheim and Ch. Schütte. *Quantum-classical molecular dynamics as an approximation to full quantum dynamics.* J. Chem. Phys., 105:1074-1083, 1996.

[Ehr27] P. Ehrenfest. *Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik.* Zeitschrift für Physik, 45:455, 1927.

[Eva10a] L.C. Evans. *Partial Differential Equations.* Second edition, American Mathematical Society, 26-33, 2010.

[Eva10b] L.C. Evans. *Partial Differential Equations.* Second edition, American Mathematical Society, 253-310, 2010.

[FK09] G. Friesecke and M. Koppen. *On the Ehrenfest theorem of quantum mechanics.* J. Math. Phys., 50:082102, 2009.

[FS10] G. Friesecke and B. Schmidt. *A sharp version of Ehrenfest's theorem for general self-adjoint operators.* Proc. Roy. Soc. A, 2010.

[GS03] S.J. Gustafson and I.M. Sigal. *Mathematical concepts of quantum mechanics.* Springer, Heidelberg, 1-29, 2003.

[Hil73] R.N. Hill. *A paradox involving the quantum mechanical Ehrenfest theorem.* American Journal of Physics, 41(5): 736-738, 1973.

[HS96a] P.D. Hislop and I.M. Sigal. *Introduction to spectral theory with applications to Schrödinger operators.* Springer, New York, 1996.

[HS96b] P.D. Hislop and I.M. Sigal. *Introduction to spectral theory with applications to Schrödinger operators.* Springer, New York, 78-81, 1996.

[HS96c] P.D. Hislop and I.M. Sigal. *Introduction to spectral theory with applications to Schrödinger operators.* Springer, New York, 131-136, 1996.

[Hun66] W. Hunziker. *On the space-time behavior of Schrödinger wavefunctions.* J. Math. Phys., 7:300-304, 1966.

[Sch02] F. Schwabl. *Quantenmechanik.* 6. Auflage, Springer, Berlin, 174-182, 2002.

[Sto32] M.H. Stone. *On one-parameter unitary groups in Hilbert space.* Annals of Mathematics 33, 3:643-648, 1932.

[Wer00a] D. Werner. *Funktionalanalysis.* 3. Auflage, Springer, Berlin, 45-58, 2000.

[Wer00b] D. Werner. *Funktionalanalysis.* 3. Auflage, Springer, Berlin, 181-193, 2000.

[Wer00c] D. Werner. *Funktionalanalysis.* 3. Auflage, Springer, Berlin, 312-349, 2000.