Mathematics

A Trigonometric Sum Relevant to the Non–relativistic Theory of Atoms

quantum mechanics/trace formulas/Weyl sums

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Abstract. We extend Van der Corput's method for exponential sums to study an oscillatory term appearing in the quantum theory of large atoms. We obtain an interpretation in terms of classical dynamics and we produce sharp asymptotic upper and lower bounds for the oscillations.

A non–relativistic atom of nuclear charge Z fixed at the origin, and N quantized electrons at positions $x_i \in \mathbf{R}^3$ is described by the Hamiltonian

$$H_{Z,N} = \sum_{i=1}^{N} \left(-\Delta_{x_i} - \frac{Z}{|x_i|} \right) + \tfrac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|}$$

which acts on the Hilbert space of antisymmetric functions with two spins

$$\mathcal{H} = \bigwedge^{N} L^2 \left(\mathbf{R}^3 \times \mathbf{Z}_2 \right).$$

In the present discussion we will ignore spin; this reduction simplifies our exposition and changes no ideas.

The ground state energy of such a system is given by

$$E(Z) = \inf_{N \geq 0} E(Z,N), \qquad E(Z,N) = \inf_{\substack{\phi \in \mathcal{H} \\ \|\phi\|=1}} \langle H_{Z,N}\phi, \phi \rangle .$$

As Z goes to infinity, the energy $E(Z)$ admits an asymptotic expansion of the form

$$E(Z) = -c_{\mathrm{TF}} Z^{7/3} + \tfrac{1}{8} Z^2 - c_s Z^{5/3} + O\left(Z^{\frac{5}{3}-a} \right), \qquad a > 0.$$

The first term above was introduced by Thomas and Fermi in (1), (2), and proved rigorously in (3) (See also (4) for a review of Thomas–Fermi theory). The Z^2 term was discovered by Scott in (5) and proved to be true in a series of papers by Hughes–Siedentop–Weikard, in (6), (7), (8) and (9). The $Z^{5/3}$ term was obtained by Schwinger in (10), and proved to be correct in (11), (12), (13), (14), (15), (16), (17) and (18).

In view of (11 — 18), it is naturally conjectured (see (19)) that the next term in the energy asymptotics for $E(Z)$ above is given by the following sum

$$\Psi_Q(Z) = \sum_{l=1}^{l_{\mathrm{TF}}} \frac{2l+1}{\displaystyle \frac{1}{\pi} \int \left(V^Z_{\mathrm{TF}}(r) - \frac{l(l+1)}{r^2} \right)_+^{-1/2} dr} \, \mu \left(\frac{1}{\pi} \int \left(V^Z_{\mathrm{TF}}(r) - \frac{l(l+1)}{r^2} \right)_+^{1/2} dr \right)$$

where $\mu(x) = \operatorname{dist}(x, \mathbf{Z})^2 - \frac{1}{12}$, V^Z_{TF} is the Thomas–Fermi potential for an atom with charge Z (see (4)), which satisfies the perfect scaling condition

$$V^Z_{\mathrm{TF}}(r) = Z^{4/3} V^1_{\mathrm{TF}} \left(Z^{1/3} \cdot r \right)$$

where we have

$$V^1_{\mathbf{TF}}(r) = \frac{y(a\cdot r)}{r}, \qquad a = \left(\frac{3\pi}{2}\right)^{2/3}$$

and y is the Thomas–Fermi function, solution of the Thomas–Fermi equation

$$\left.\begin{aligned} y''(r) &= \frac{y^{3/2}(r)}{r^{1/2}} \\ y(0) &= 1 \\ \lim_{r\to\infty} y(r) &= 0 \end{aligned}\right\}$$

Finally, $l_{\mathbf{TF}}$ is the greatest integer such that $V^Z_{\mathbf{TF}}(r) - l(l+1)/r^2$ is positive somewhere.

The book of Englert ((20); see also references thereof) contains a discussion of oscillatory terms in the asymptotics of $E(Z)$.

The purpose of this paper is to analyze the sum $\Psi_Q(Z)$ as a function of Z. Note that, although in our application Z ranges over the integers, the same definition of Ψ_Q extends naturally to all real values of Z.

In order to explain our main result, consider a classical particle with mass $\frac{1}{2}$, moving in the negative radial potential given by $-V^Z_{\mathbf{TF}}$. Such motion is planar, and we consider the closed orbits which arise for angular momentum M; first, all orbits can be obtained from a *primitive* one that we travel through k times, for k any non–zero integer which we call *multiplicity.* All such orbits for a fixed M with the same multiplicity can be obtained by rotations of each other. On each of those orbits, the particle "oscillates" in the sense that the distance to the origin $r(t)$ varies between $r_{\mathbf{min}}(M)$ and $r_{\mathbf{max}}(M)$ and closes after passing $n(M)$ times through, say, $r_{\mathbf{max}}(M)$. We also consider the integer $l(M)$, the winding number of the orbit around 0, the action $S(M)$, the period $T(M)$, and the following locally defined quantity: for a closed trajectory with angular momentum M, and n oscillations, and given ε small, consider a trajectory (not necessarily closed) with angular momentum $M+\varepsilon$ which, after $n(M)$ oscillations between successive $r_{\mathbf{max}}(M+\varepsilon)$, misses to close by an angle $2\pi\alpha_M(\varepsilon)$, where we take α between 0 and 1. Then, we define

$$D(M) = \lim_{\varepsilon\to 0} \varepsilon^{-1}\alpha_M(\varepsilon)$$

This description degenerates for the maximum angular momentum $M_{\mathbf{max}}$, which gives rise to a single circular primitive orbit, together with its corresponding multiples. In this case, numbers l and n can be naturally extended as follows: set

$$\phi(\Omega) = \int \left(\frac{y(r)}{r} - \frac{\Omega^2}{r^2} \right)_+^{1/2} dr \tag{1}$$

for $\Omega \in (0, \Omega_c)$ with $\phi(\Omega_c) = 0$. Then if $\frac{1}{\pi}\phi'(\Omega_c)$ is irrational, we set $n = \infty$. Otherwise, we set $\frac{1}{\pi}\phi'(\Omega_c) = -l/n$, with different choices of l and n translating into the same circle with different multiplicities. Primitive representations correspond to the case that l and n are relatively prime. $D(M_{\mathbf{max}})$ can still be defined the same way by taking $\varepsilon < 0$ in our definition above when n is finite; when n is infinite, there will be no need for us to define $D(M_{\mathbf{max}})$.

With this notation, our main result is as follows:

Theorem 1:

$$\Psi_{\boldsymbol{Q}}(Z) = \Psi_{\mathbf{0}}(Z) + o\left(Z^{3/2}\right)$$

where

$$\Psi_{\mathbf{0}}(Z) = 2\pi \cdot Z^{3/2} \cdot \sum_{\textbf{closed trajectories}} \delta \, \frac{\hat{\mu}(n) \cdot n \cdot M}{T} \cdot |D(M)|^{-1/2} \cdot e^{i\left(Z^{1/3} S - \pi \cdot (l + \frac{\textbf{sign } n}{4})\right)}$$

where $\delta = 1$ *except in the case of an exactly circular orbit, when* $\delta = \frac{1}{2}$. *Furthermore, the sum is absolutely convergent.*

As a consequence of the same methods used to prove this theorem we obtain the following estimate for the size of $\Psi_{\boldsymbol{Q}}(Z)$

Theorem 2: *There are universal constants* K *(large) and* κ_0 *(small but strictly positive), such that*

$$|\psi_{\boldsymbol{Q}}(Z)| \le K \cdot Z^{3/2}, \qquad \text{and} \qquad \int_{Z_0}^{Z_0+Z} |\psi_{\boldsymbol{Q}}(z)|^2 \, \frac{dz}{z^3} \ge \kappa_0 \cdot Z$$

whenever $Z \ge K \, Z_0^{2/3}$. *Furthermore,*

$$\liminf_{\substack{Z \to \infty \\ Z = 1,2,3,\ldots}} \left| Z^{-3/2} \psi_{\boldsymbol{Q}}(Z) \right| \ne 0.$$

1. Comments on the Proof

The proof of our theorem is a variant of a method devised by Van der Corput (see (21)) to study trigonometric sums appearing in different number theoretic problems. Of special interest to us is the lattice point problem, which consists in estimating the number of lattice points inside a large convex region.

According to this method, a sum like ours, after Poisson summation, becomes a sum of Fourier integrals. Each integral can be expanded via the stationary phase method to become a sum of complex exponentials with real amplitudes. This gives the leading expression Ψ_0, together with the upper bound, where we take advantage of the fast decrease of the Fourier coefficients of μ. The lower bound requires some extra work, and hinges on the fact that a certain number is not zero. After all this, the connection with closed trajectories is an exercise in classical mechanics.

Our result appears to have certain similarities with another recent result of P. Bleher (22). The book of Gutzwiller (23) contains a discussion of the interplay between classical and quantum mechanics in relation with trace formulas.

The trigonometric sums involved in the analysis of the lattice point problem have similarities with our sum, with the crucial difference that the corresponding μ there is $x - [x] - \frac{1}{2}$, whose Fourier coefficients decay merely like n^{-1}: this is responsible for the fact that to obtain sharp bounds for this problem remains a hard open question. More concretely, one can consider sums given by

$$P = \sum_{k=1}^{N} \mu\left(N\phi(\frac{k}{N})\right)$$

where μ is a periodic function of average 0. Examples of such sums are the ones given by

$$\hat{\mu}(n) = n^{-s}, \qquad s = \sigma + i\tau$$

The case $s = 1$ is the lattice point problem for the dilates of the curve $\phi(x)$. Our sum corresponds to the case $s = 2$.

A crucial ingredient in our analysis is the non–degeneracy of the Thomas–Fermi potential (proved in (18)), which, from the analytical point of view, means that

$$|\phi''(\Omega)| > c_0 > 0$$

for a constant c_0 and ϕ as in (1). In the classical formalism, it amounts to the fact that $D(M) \neq 0$ for all closed trajectories. This means that closed trajectories are isolated once we factor out the trivial symmetry given by the rotation group. Its role in the proof is similar to the non–vanishing curvature of the sphere in the circle problem.

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