Atoms and Analytic Number Theory

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In this brief, expository article I will explain some recent work on a mathematical problem arising from the elementary quantum mechanics of atoms and molecules. That problem is to compute the ground-state energy of a single atom with large atomic number Z. To account for chemical phenomena, one wants a very accurate determination of the ground-state energy $E(Z)$ and its analogue for molecules. Unfortunately, such great accuracy is more than we can achieve today. Nevertheless, there has been interesting recent progress. In particular, L. Seco and I have rigorously computed $E(Z)$ with a percentage error $o(Z^{-2/3})$; and Ivrii and Sigal have rigorously computed the analogue of $E(Z)$ for a molecule with a percentage error $o(Z^{-1/3})$. This article picks out one aspect of the recent work, namely the connection of the asymptotics of $E(Z)$ to analytic number theory. More generally, number-theoretic questions arise whenever one asks for precise asymptotics for a quantum-mechanical problem with many particles. Let us see this in the simplest possible quantum system, namely N free particles in a box. Then we will return to atoms.

Imagine, then, N free particles in a box $Q = [-\pi, \pi]^3 \subset \mathbb{R}^3$. We assume the particles obey Fermi statistics. What is the lowest possible kinetic energy $KE(N)$ for the N particles? The problem is an exercise in elementary mathematics. We are trying to minimize $\int_{Q^N} (-\Delta\psi)\overline{\psi}\,dx_1 \cdots dx_N$ over all wave functions $\psi(x_1, \ldots, x_N) \in L^2(Q^N)$ of norm 1, which satisfy the antisymmetry condition $\psi(x_{\sigma_1}, \ldots, x_{\sigma_N}) = (\mathrm{sgn}\,\sigma)\psi(x_1, \ldots, x_N)$ for permutations σ. (Here we ignore spin. This simplifies notation and changes a few coefficients, but does not affect the essential ideas.)

The problem is easily solved by separation of variables and the lowest kinetic energy is simply the least possible sum of the form $|\xi_1|^2 + \cdots + |\xi_N|^2$, where $\xi_1, \ldots, \xi_N$ are distinct lattice points in $\mathbb{R}^3$. Moreover, it is geometrically obvious how to place N lattice points to minimize the sum of

the squares of their norms. We simply pick a ball $B(0, R) \subset \mathbb{R}^3$, containing at least N lattice points in its closure, but at most N in its interior. Our $\xi_1, \dots, \xi_N$ merely consist of all the lattice points in the interior of the ball, together with just enough on the bounding sphere to make a total of N points. If we are satisfied with crude asymptotics for N large, then we need only remark that the number of lattice points is approximately equal to the volume, so that

> $N \approx$ number of lattice points in $B(0, R) \approx \frac{4}{3}\pi R^3$, and Min. Kinetic Energy $\approx$ Sum of the squares of the norms of the lattice points in $B(0, R) \approx \int_{\xi \in B(0, R)} |\xi|^2 d \operatorname{vol}(\xi) = (\text{const})R^5$.

Consequently,

$$\text{Min. Kinetic Energy} \approx (\text{const}')N^{5/3},$$

as is well known to anyone interested in quantum mehanics. However, if we want to know more precise information on the minimum kinetic energy, then clearly we need to know the number of lattice points in a ball of radius R. This is a classical problem of analytic number theory. So, already for free particles in a box, we encounter number theory if we ask for precise information. In more complicated quantum-mechanical systems such as a large atom, number-theoretic issues are still present.

Let me recall very briefly what is known about lattice points in a ball. Trivially, a ball $B(0, R)$ in $\mathbb{R}^n$ contains $\omega_n R^n + O(R^{n-1})$ lattice points, where ω_n is the volume of the unit ball. The error term simply counts the number of lattice points within distance $O(1)$ of the boundary. However, the trivial error term can be improved. Hardy showed in 1913 that the number of lattice points in a disc of radius R is $\pi R^2 + O(R^{2/3})$. The best error term in two dimensions is conjectured to be $O(R^{1/2+\varepsilon})$, but only slight improvements on Hardy's result are known at present. All we need for our present work on quantum mechanics is to improve the trivial error term to $O(R^{n-1-\varepsilon})$. Thus, Hardy's result is enough for the moment.

Hardy's work relies crucially on the fact that the circle is curved. If we try to count the lattice points in a large square of side R, then the obvious estimate $R^2 + O(R)$ will be best possible. Hardy's result generalizes from the circle to any domain in $\mathbb{R}^n$ with a smooth boundary whose principal curvatures never vanish. Improvements over Hardy's theorem are special for the circle.

Now I will return to atoms, and sketch the heuristic picture of a large atom, discovered by the physicists. We are trying to find the lowest eigenvalue $E(Z)$ of the Hamiltonian

$$(1) \qquad H = \sum_{k=1}^{Z} \left(-\Delta_{x_k} - \frac{Z}{|x_k|} \right) + \sum_{i \leq j < k \leq Z} \frac{1}{|x_j - x_k|},$$

acting on antisymmetric functions $\psi(x_1, \ldots, x_Z) \in L^2(\mathbb{R}^{3Z})$. This problem is hard because of the term $\sum 1/|x_j - x_k|$, in which the electrons interact. If our Hamiltonian had the form

$$(2) \qquad H_0 = \sum_{k=1}^{Z} (-\Delta_{x_k} + V(x_k))$$

for a one-electron potential V, then by separation of variables the problem would reduce from $3Z$ to three dimensions. In fact, exploiting the sphereical symmetry, we would really be dealing merely with one-dimensional problems (ODEs). The main idea used to study atoms in physics and chemistry is to approximate (1) by (2), with $V(x)$ picked as follows: Pretend for a moment that we know the particle density $\rho(x)$ for the electrons. Thus, $\rho(x)$ is defined on $\mathbb{R}^3$, and the integral of ρ over a set $\Omega \subset \mathbb{R}^3$ is equal to the expected number of electrons found in Ω, according to the full probability density

$$d \text{ Prob} = |\psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N.$$

Here ψ is the ground-state eigenfunction for H.

Once we know ρ, we can cook up a potential $V(x)$ for which H_0 is a good approximation for H. In fact, we just take

$$(3) \qquad V(x) = -\frac{Z}{|x|} + \int_{\mathbb{R}^3} \frac{\rho(x)\, dy}{|x - y|}.$$

If the electrons act more or less independently, then each electron x_k feels the repulsion from all other electrons approximately as if it were being repelled by a fixed, continuous charge distribution ρ. Hence it is plausible that H should be well approximated by H_0. (Actually, H should be approximated not by H_0 but by $H_0 -$ (Large Constant). We suppress a careful discussion of this point.)

The *Hartree-Fock* approximation approximates the ground-state eigenfunction for H by that of H_0. The ground-state eigenfunction for H_0 which we call $\psi_{\text{hf}}(x_1, \ldots, x_N)$, can of course be written explicitly as an anti-symmetrized product of the eigenfunctions $\varphi_1(x), \ldots, \varphi_N(x)$ for the three-dimensional Schrödinger operator $-\Delta + V(x)$.

Once we have a guess ψ_{hf} for the ground-state eigenfunction, we can then produce a guess for the lowest eigenvalue $E(Z)$, merely by taking

$$E_{\text{hf}}(Z) = \langle H\psi_{\text{hf}}, \psi_{\text{hf}} \rangle.$$

This is an immense simplification over the original problem, because we are dealing with a three-dimensional problem instead of a $3Z$-dimensional one. To make it work, we need to decide which density $\rho(x)$ to start with. Fortunately, the Hartree-Fock approximation leads to a natural equation for ρ. In fact, the Hartree-Fock wave function $\psi_{\text{hf}}(x_1, \ldots, x_N)$ gives rise to its own particle density $\rho_{\text{hf}}(x)$ on $\mathbb{R}^3$. In terms of the eigenfunctions φ_k of

$-\Delta + V(x)$ on $\mathbb{R}^3$, ρ_{hf} is simply

$$\rho_{\mathrm{hf}}(x) = \sum_{k=1}^{N} |\varphi_k(x)|^2.$$

We call this the Hartree-Fock density arising from ρ. To get a self-consistent approximation, we demand that $\rho_{\mathrm{hf}}(x) = \rho(x)$, i.e., the density we produce must equal the density we started with. This is the Hartree-Fock equation. To recapitulate, $\rho(x)$ gives rise to $V(x)$ by (3); from $V(x)$ we produce the eigenfunctions $\varphi_1(x), \ldots, \varphi_N(x)$ of $-\Delta + V(x)$; and we demand that ρ be picked so that $\rho_{\mathrm{hf}} = \sum_{k=1}^{N} |\varphi_k|^2$ will be equal to ρ. This is a rather strange equation. It certainly is not a partial differential equation or an integral equation in the usual sense. To solve it in practice, physicists and chemists use the following successive approximation scheme: Suppose we can produce a reasonable initial guess ρ_0 for the unknown particle density. Then we can successively define ρ_1, ρ_2, ... by taking ρ_{k+1} to be the Hartree-Fock density arising from ρ_k. This appears in practice to lead to satisfactory approximate solutions to the Hartree-Fock equation after a few steps. It is certainly not immediately obvious why it should work. It is also not immediately obvious how to produce a good initial guess ρ_0. One way to find a ρ_0 is to use the Thomas-Fermi theory, which we now describe.

Thomas-Fermi theory is based on approximations to the density and eigenvalue sum of a three-dimensional Schrödinger operator $-\Delta + V(x)$. If E_k are the negative eigenvalues of $-\Delta + V(x)$ and $\varphi_k(x)$ are the corresponding eigenfunctions, then we want to approximate $\mathrm{sneg}(V) = \sum_k E_k$ and $\rho_{\mathrm{hf}}(x) = \sum_k |\varphi_k(x)|^2$. These are the important quantities for us, since $\mathrm{sneg}(V)$ is the lowest possible energy for the Hamiltonian (2), and ρ_{hf} is one side of the Hartree-Fock equation that determines the density. The *semiclassical approximations* are

$$(4) \qquad \mathrm{sneg}(V) \approx -(\mathrm{const}) \int_{V<0} |V|^{5/2} \, dx,$$

$$(5) \qquad \rho_{\mathrm{hf}}(x) \approx (\mathrm{const}) |V(x)|^{3/2} \chi_{V(x)<0}.$$

These approximations work well when $V(x)$ is large and rather slowly varying, e.g., $V(x) = \lambda^2 V_0(x)$, with $V_0(x)$ fixed and smooth and $\lambda \gg 1$. To prove (4) and (5), one can follow the same ideas introduced by H. Weyl to prove that the number of eigenvalues $< \lambda$ for the Laplacian on a domain $\Omega \subset \mathbb{R}^n$ is asymptotic to $c_n \lambda^{n/2} \mathrm{vol}\,\Omega$ when $\lambda \to \infty$.

Using the semiclassical approximations, we can rewrite the Hartree-Fock equation $\rho_{\mathrm{hf}} = \rho$ in the much more pleasant form

$$(6) \qquad \rho(x) = (\mathrm{const}) \cdot (-V(x))^{3/2}.$$

(We expect that $V(x)$ will be negative on $\mathbb{R}^3$, so (5) leads to (6).) Equations (3) and (6) make up a coupled system of equations for the potential V

and density ρ. It is trivial to eliminate either V or ρ from the equation using (6), so that we get a single integral equation for (say) ρ. Taking the Laplacian of both sides, we then get a (nonlinear) partial differential equation for ρ. Since ρ is expected to be spherically symmetric, equations (3) and (6) finally reduce to an ordinary differential equation. Thus, the density ρ and potential V may be read off from ordinary differential equations. These ρ and V represent the semiclassical approximations to the Hartree-Fock approximation to the real atom. They are called the Thomas-Fermi density ρ_{TF} and the Thomas-Fermi potential V_{TF}. The parameter Z in equations (3) and (6) may be removed by a trivial scaling, and therefore

$$(7) \qquad \rho_{TF}(x) = Z^2 \rho_1(Z^{1/3}x),$$

$$(8) \qquad V_{TF}(x) = Z^{4/3} V_1(Z^{1/3}x)$$

for universal functions ρ_1 and V_1, which may be found by solving ordinary differential equations. Putting (8) into (4), we obtain $\mathrm{sneg}(V_{TF}) \approx -(\mathrm{const})Z^{7/3}$. Thus we have computed the ground-state energy for the Hamiltonian (2). After taking into account the additive constant mentioned just after (3), we obtain the Thomas-Fermi approximation to the ground-state energy of an atom, namely

$$(9) \qquad E(Z) \approx -c_{TF}Z^{7/3}.$$

As noted in the introduction, we need highly accurate approximations to $E(Z)$. The Thomas-Fermi approximation (9) is very crude. Using heuristic methods, physicists found a closer approximation than (9) to the Hartree-Fock energy, namely

$$(10) \qquad E(Z) \approx -c_{TF}Z^{7/3} + \tfrac{1}{8}Z^2 - c_{DS}Z^{5/3}.$$

Of course, the Hartree-Fock energy itself is only an approximation to the true ground-state energy $E(Z)$.

I will not take the time to give a complete account of the ideas that led to (10), but I want to single out one part of the argument, namely a proposed refinement of (4) and (5) due to Schwinger [6]. Schwinger's formulas are as follows:

$$(11) \qquad \mathrm{sneg}(V) \approx -(\mathrm{const}) \int_{V<0} |V|^{5/2}\,dx + (\mathrm{const}') \int_{V<0} (\Delta V)|V|^{1/2}\,dx,$$

$$(12) \qquad \rho_{hf}(x) \approx \chi_{V(x)<0} \cdot \{(\mathrm{const})|V(x)|^{3/2} + (\mathrm{const}')(\Delta V) \cdot |V(x)|^{-1/2}$$
$$- (\mathrm{const}'')|\nabla V|^2 |V(x)|^{-3/2}\}.$$

Schwinger found these formulas by trying to guess the general case from the example of the harmonic oscillator $-d^2/dx^2 + \lambda^2 x^2$ in one dimension. Formula (11) has to be modified when V contains a Coulomb singularity. This concludes our sketch of the atom according to physicists.

Next we turn to rigorous results. An excellent survey of what was known up to about 1980 is contained in Lieb [3]. The main result then known on atoms was the theorem of Lieb-Simon [5] that $E(Z) = -c_{TF}Z^{7/3} + O(Z^a)$ with an explicit a between $\frac{7}{3}$ and 2. The proof was very much in the spirit of Weyl's work on eigenvalues. It applies also to molecules. An important unsolved problem was to prove the "Scott conjecture," i.e., $E(Z) = -c_{TF}Z^{7/3} + \frac{1}{8}Z^2 + O(Z^a)$ with $a < 2$. This was settled by Hughes [2] and Siedentop-Weikard [7] in the mid-1980s. Recently, there has been further progress. Specifically, Ivrii and Sigal have proven the analogue of the Scott conjecture for a molecule; and L. Seco and I have proven [1] that

$$\text{(12a)} \qquad E(Z) = -c_{TF}Z^{7/3} + \tfrac{1}{8}Z^2 - c_{DS}Z^{5/3} + O(Z^a)$$

for an $a < \frac{5}{3}$ for atoms, justifying (10). It would be very interesting to combine the two results into a rigorous computation of the energy of a molecule modulo $o(Z^{5/3})$. It would also be interesting to write down the next correction term beyond $Z^{5/3}$ in the asymptotic behavior of $E(Z)$. Our work suggests the form of the next term, but is not strong enough to prove it. The next term in $E(Z)$ is not $Z^{4/3}$ as one might expect, but rather a series from analytic number theory. That series is closely related to lattice point problems. It fluctuates as a function of Z, and is not proportional to any power of Z. Similar fluctuations occur already for free particles in a box.

How can one produce rigorous upper and lower bounds for $E(Z)$? In principle, upper bounds are easy. Starting from the Thomas-Fermi density ρ_{TF} and its potential V_{TF}, we form the Hartree-Fock wave function[1] $\psi_{hf}(x_1, \ldots, x_N)$ by taking the antisymmetrized product of the eigenfunctions $\varphi_1(x), \ldots, \varphi_N(x)$ of $-\Delta + V_{TF}$ on $\mathbb{R}^3$. We think but do not know that ψ_{hf} is close to the true ground-state. To make an upper bound for $E(Z)$, we have only to calculate the inner product $\langle H\psi_{hf}, \psi_{hf}\rangle$, with H given by (1). Minimax tells us that this inner product is a rigorous upper bound for $E(Z)$, whether or not ψ_{hf} is close to the true ground-state. If our opinions are correct, our upper bound will turn out to be quite sharp.

Producing lower bounds for $E(Z)$ is much harder. Instead of computing $\langle H\psi, \psi\rangle$ for a single wave function ψ, we need to prove a lower bound for $\langle H\psi, \psi\rangle$ with an arbitrary antisymmetric ψ. The usual starting point, which goes back to Lieb [4], is to prove an inequality of the form

$$\text{(13)} \qquad \sum_{i<j} \frac{1}{|x_i - x_j|} \geq \sum_{i=1}^{N} W(x_i) - C_0$$

for a suitable one-electron potential W and constant C_0.

Once such an inequality is known, it follows that the true Hamiltonian H

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[1] Actually, it is enough to form ψ_{hf} by *guessing* the eigenfunctions of $-\Delta + V$.

in (1) satisfies

$$H \geq \sum_{k=1}^{Z} \left(-\Delta_{x_k} - \frac{Z}{|x_k|} + W(x_k) \right) - C_0.$$

The right-hand side contains no interactions, and hence may be understood by separation of variables. Thus, $E(Z) \geq \text{sneg}(-Z/|x| + W) - C_0$, so that we have a rigorous lower bound for the ground-state energy. Whether this lower bound is sharp or useless depends on our skill in picking and proving a good inequality of the form (13). I will explain one way to prove (13) that leads to reasonable results. The starting point is an elementary observation, namely

$$(14) \qquad |x - x'|^{-1} = \frac{1}{\pi} \int_{\substack{y \in \mathbb{R}^3 \\ R > 0}} \chi_{x, x' \in B(y, R)} \frac{dy \, dR}{R^5} \quad \text{for } x, x' \in \mathbb{R}^3.$$

Except for the fact that the coefficient here is $\frac{1}{\pi}$, this equation follows merely by noting that both sides have the same invariance under translations, rotations, and dilations. Taking $x = x_j$, $x' = x_k$ in (14) and summing over all possible pairs of particles, we see that

$$(15) \qquad \sum_{i < j} |x_i - x_j|^{-1} = \frac{1}{\pi} \int_{\substack{y \in \mathbb{R}^3 \\ R > 0}} \frac{N(y, R)(N(y, R) - 1)}{2} \frac{dy \, dR}{R^5}$$

for any $x_1, \ldots, x_N \in \mathbb{R}^3$, with $N(y, R) = $ number of $x_j \in B(y, R) = \sum_j \chi_{B(y, R)}(x_j)$.

The next step is to make a guess $\overline{N}(y, R)$ for the number of electrons in $B(y, R)$. For instance, we may take

$$(16) \qquad \overline{N}(y, R) = \int_{B(y, R)} \rho_{\text{TF}}.$$

We believe (but do not know) that this guess is a good one. Using $\overline{N}(y, R)$, we rewrite the integrand in (15) as

$$(17) \quad \begin{aligned} \tfrac{1}{2} N(y, R)(N(y, R) - 1) &= \tfrac{1}{2} [N(y, R) - \overline{N}(y, R)]^2 \\ &\quad + [\overline{N}(y, R) - \tfrac{1}{2}] N(y, R) - \tfrac{1}{2} [\overline{N}(y, R)]^2. \end{aligned}$$

When we substitute (17) into (15), the term $[\overline{N}(y, R) - \tfrac{1}{2}] N(y, R)$ contributes something of the form $\sum_k W(x_k)$ to the energy, because $N(y, R) = \sum_k \chi_{B(y, R)}(x_k)$ and $\overline{N}(y, R)$ are independent of the x_k. The term $-\tfrac{1}{2} [\overline{N}(y, R)]^2$ in (17) is also independent of the x_k, and hence merely contributes an additive constant to the energy.

The part of (17) that is hard to understand is $[N(y, R) - \overline{N}(y, R)]^2$. We can get a cheap lower bound, simply by discarding this positive term and writing

$$(18) \qquad \tfrac{1}{2} N(y, R)[N(y, R) - 1] \geq [\overline{N}(y, R) - \tfrac{1}{2}] N(y, R) - \tfrac{1}{2} [\overline{N}(y, R)]^2.$$

If our guess $\overline{N}(y, R)$ was intelligent and if $B(y, R)$ is likely to contain many electrons, then $[N(y, R) - \overline{N}(y, R)]^2$ should be negligibly small compared to $\frac{1}{2}N(y, R)[N(y, R) - 1]$. Hence (18) may provide useful information.

However, if $B(y, R)$ is small enough, then it will probably contain either 0 or 1 electrons. In this case, $\overline{N}(y, R) \ll 1$, $N(y, R) = 0$ or 1, and $[N(y, R) - \overline{N}(y, R)]^2$ is not negligible compared to $\frac{1}{2}N(y, R)[N(y, R) - 1]$, so that using (18) is a bad idea. For small $B(y, R)$ it is better just to use the trivial lower bound $\frac{1}{2}N(y, R)[N(y, R) - 1] \geq 0$. Therefore, we set

$$E = \{(y, R) | \overline{N}(y, R) > 1\}$$

(say), and we conclude from (15) and (18) that

$$\sum_{i<j} |x_i - x_j|^{-1} \geq \frac{1}{\pi} \int_{(y, R) \in E} \left[\overline{N}(y, R) - \frac{1}{2} \right] N(y, R) \frac{dy \, dR}{R^5}$$

$$- \frac{1}{\pi} \int_{(y, R) \in E} \frac{1}{2} [\overline{N}(y, R)]^2 \frac{dy \, dR}{R^5}.$$

The first integral on the right has the form $\sum_k W(x_k)$, and the second integral is an additive constant C_0. Hence we have succeeded in proving an inequality of the form (13). If we define $\overline{N}(y, R)$ intelligently, e.g., by (16), then the resulting inequality (13) leads to a lower bound for $E(Z)$ strong enough to prove the Scott conjecture.

Let us summarize the preceding discussion. Upper bounds for $E(Z)$ are proved by using the Hartree-Fock approximate ground-state ψ_{hf} as a trial wave function. Lower bounds are proved by invoking (13) to obtain an inequality $H \geq \sum_k (-\Delta_{x_k} + V(x_k)) - C_0$. The right-hand side can be understood by separation of variables. Of course, it takes lots of hard work to understand $-\Delta + V(x)$ on $\mathbb{R}^3$ with enough precision to carry this out. For atoms, the hard work deals with ODE's since $V(x)$ is spherically symmetric. To get the Scott conjecture for a molecule, one needs instead to understand a genuinely three-dimensional problem.

In a sense, we have been lucky so far. The original problem is $3Z$-dimensional with $Z \to \infty$, yet we have not had to look seriously at any quantum-mechanics problem in dimension greater than 3. The reason for the good luck is that we could drop the only difficult term, $[N(y, R) - \overline{N}(y, R)]^2$, from (17), and thus bound the true Hamiltonian from below by a noninteracting one. The contribution of that term to the total energy is of the order of magnitude $Z^{5/3}$, when $\overline{N}(y, R)$ is picked optimally. Hence, we can reduce matters from $3Z$ dimensions to three, provided we are willing to ignore errors $O(Z^{5/3})$ in the energy. This is good enough for the Scott conjecture, but not for (12a). In proving (12a) we are forced for the first time to come to grips with the quantum mechanics of an interacting system. This is perhaps the main point in our proof of (12a), but we will not discuss it further here.

Instead, we turn to the Schwinger formulas (11) and (12), which must be rigorously understood before one can hope to derive (12a). It would be very

interesting to give a rigorous discussion of the Schwinger formulas for rather general V in three dimensions. What Seco and I did was much easier. We understood the spherically symmetric case by making a very precise analysis of the eigenvalues and eigenfunctions of ordinary differential equations. This is of course good enough for an atom, but not for a molecule. The details of our work on ODE's are long and complicated. In the end, we derive formulas for $\mathrm{sneg}(V)$ and ρ_{hf} analogous to (11) and (12). However, in addition to the terms displayed on the right in (11) and (12), there are number-theoretic series related to the lattice-point problem. We are not surprised to see such series, in view of the example of N free particles. Thus, (11) and (12) are correct, provided the number-theoretic terms are negligibly small. In (12), this is simply not the case. The number-theoretic terms actually dominate over Schwinger's correction terms, and (12) is wrong, at least for radial potentials. One important point in our proof of (12a) is therefore to use only relatively crude asymptotics for ρ_{hf}, in order to get away without (12).

The role of the number-theoretic series in (11) is less destructive. If we estimate it by trivial methods, analogous to the trivial $\pi R^2 + O(R)$ for the number of lattice points in a disc, then we see that the series is at most of the same order of magnitude as Schwinger's correction term in (11). So to prove (11), we need to make a small improvement over the trivial estimate of the number-theoretic sum. The analogue of Hardy's $O(R^{2/3})$ result will be enough for our purposes. However, to apply Hardy's theorem, we need nonzero curvature. The condition that plays the role of nonzero curvature here turns out to be the following.

PERIODIC ORBIT CONDITION. Form the classical Hamilitonian $H_{\mathrm{cl}} = |\vec{p}|^2 + V(\vec{q})$ for $\vec{p}, \vec{q} \in \mathbb{R}^3$. Then the set of periodic zero-energy orbits for H_{cl} has measure zero in the set of all zero-energy orbits.

The number-theoretic term in (11) can be dropped if and only if the periodic orbit condition is satisfied. Hence, Schwinger's formula for the eigenvalue sum holds for a radial potential V if and only if the periodic orbit condition is satisfied. The connection of sharp eigenvalue asymptotics to periodic orbits is of course an old story in the context of the Laplacian on a manifold. The connection to periodic orbits clearly points to wave equation methods in any future attempt to understand nonradial V.

The periodic orbit condition fails with a vengeance for the harmonic oscillator, where the whole Hamiltonian flow is periodic. Thus (11) fails there also, as the reader may check by elementary computation. It is remarkable that Schwinger correctly guessed (11) by thinking hard about one of the few examples in which it is false.

After repeatedly discussing unspecified number-theoretic sums, we close by writing down the series that we believe forms the next term in $E(Z)$ beyond $Z^{5/3}$.

Let $V_{\mathrm{TF}}(r)$ be the Thomas-Fermi potential for atomic number Z. For

$l \geq 0$, set $V_l(r) = l(l+1)/r^2 + V_{\mathrm{TF}}(r)$. Then define

$$\eta_l = \int_{\{V_l < 0\}} |V_l(r)|^{-1/2}\, dr \quad \text{and} \quad \phi_l = \frac{1}{\pi} \int_{\{V_l < 0\}} |V_l(r)|^{+1/2}\, dr.$$

Let $\beta(t) = |t - k|^2 - \frac{1}{12}$, where k is the integer nearest to t. Our conjecture is that

$$E(Z) \approx -c_{\mathrm{TF}} Z^{7/3} + \frac{1}{8} Z^2 - c_{\mathrm{DS}} Z^{5/3} + (\text{const}) \sum_{l \geq 1} \frac{(2l+1)}{\eta_l} \beta(\phi_l).$$

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