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EQUATIONS AUX DERIVEES PARTIELLES

SEMICLASSICAL ASYMPTOTICS FOR EXCHANGE ENERGY

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SEMICLASSICAL ASYMPTOTICS FOR EXCHANGE ENERGY[†]

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In this talk I would like to present the very first results of my intervention to the *Multiparticle Quantum Theory* (MQT). A lot of nice results was obtained by mathematical physicists but the *Theory of Semiclassical Spectral Asymptotics* (TSSA) was applied only in a few papers and I believe that the systematic application will provide some progress. This is my long term project. However, it is vital to combine methods of TSSA and MQT.

1. General. Let us consider the following operator (quantum Hamiltonian)

$$H = \sum_{1\le j\le N} \left(\Delta_{x_j} + V(x_j)\right) + \sum_{1\le j<k\le N} |x_j - x_k|^{-1} \tag{1}$$

describing N same type particles in the external field with the potential V and repulsing one another according Coulomb law. Here $x_j \in \mathbb{R}^d$ and $(x_1,\dots,x_N) \in \mathbb{R}^{Nd}$. Δ is a positive Laplacian in $\mathbb{R}^d$, function $V(x)$ is assumed to be real-valued. Mass is equal to $\frac{1}{2}$ and Plank constant and a charge are equal to 1 here. The crucial question is the quantum statistics. We assume that the particles (electrons) are fermions. That means that the Hamiltonian should be considered on the Fock space $\mathcal{H} = \bigwedge_{1\le j\le N} L^2(\mathbb{R}^d)$ of the functions antisymmetric with respect to all variables $x_1,\dots,z_N$ while for bosons one should consider a space symmetric functions or (what is the same in our problem) on the space $\bigotimes_{1\le j\le N} L^2(\mathbb{R}^d)$ of all functions. We neglect the fact that one particle is described by the wave function $\phi \in L^2(\mathbb{R}^d,\mathbb{C}^q)$ rather than by the wave function $\phi \in L^2(\mathbb{R}^d,\mathbb{C})$. One can easily adjust our arguments to the case $q > 1$. Let us assume that

(2) Operator H is self-adjoint on $\mathcal{H}$.

We will never discuss this assumption. We are interested in the *ground state energy* $E = E(N)$ of our system i.e. in the lowest eigenvalue of the operator H on $\mathcal{H}$. The first approximation is the Hartree-Fock (or Thomas-Fermi) theory. Namely, let us introduce the space density of the particle with the state $\psi \in \mathcal{H}$:

$$\rho(x) = N \int |\psi(x, x_2,\dots,x_N)|^2 dx_2 \cdots dx_N \tag{3}$$

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(antisymmetricity of ψ implies that it doesn't matter what variable x_j is replaced by x). Let us write the Hamiltonian, describing the corresponding "quantum liquid":

$$\mathcal{E}(\rho) = \varkappa \int \rho^{1+\frac{2}{d}} dx + \int V\rho dx + \frac{1}{2}\iint |x-y|^{-1}\rho(x)\rho(y)dxdy \tag{4}$$

where the numerical value of $\varkappa$ is $4\pi^2\omega_d^{-\frac{2}{d}} d(2+d)^{-1}$, ω_d is the volume of the unit ball in $\mathbb{R}^d$. The classical sense of the second and the third terms is clear and why the density of the kinetic energy is $\varkappa\rho^{1+\frac{2}{d}}$ in the semiclassical approximation will be explained later. So, the problem is to minimize this functional under restrictions

$$\rho \ge 0, \qquad \int \rho dx = N. \tag{5}$$

The solution if exists is unique because functional $\mathcal{E}(\rho)$ is strictly convex[1]. The existence and the property of this solution denoted further by ρ_{TF} is known in the series of physically important cases.

To justify the heuristic formula $E \sim \mathcal{E}_{TF} = \mathcal{E}(\rho_{TF})$ and to find the error estimate let us deduce the lower and upper estimates of E. For lower estimate we apply the *electrostatic inequality* due to E.H.Lieb (later we replace it by more precise bound due to Graf-Solovej):

$$\sum_{1\le j<k\le N} \int |x_j - x_k|^{-1} |\psi(x_1,\dots,z_N)dx_1\cdots dx_N \ge \frac{1}{2}\iint |x-y|^{-1}\rho(x)\rho(y)dxdy - C\int \rho^{1+\frac{1}{d}}dx. \tag{6}$$

This inequality holds for all (not necessarily antisymmetric) functions ψ with $\|\psi\|_{L^2(\mathbb{R}^{dN})} = 1$. Actually it was proven for $d = 3$ but generalization for $d \ge 2$ is rather trivial. So,

$$\begin{aligned}\langle H\psi,\psi\rangle \ge \sum_{1\le j\le N} \langle A_{x_j}\psi,\psi\rangle + \\ \frac{1}{2}\iint |x-y|^{-1}(\rho-\rho_{TF})(x)(\rho-\rho_{TF})(y)dxdy - \\ \frac{1}{2}\iint |x-y|^{-1}\rho_{TF}(x)\rho_{TF}(y)dxdy - C\int \rho^{1+\frac{1}{d}}dx\end{aligned} \tag{7}$$

where $\langle,\rangle$ means the inner product in $\mathcal{H}$ and A is one-particle Schrödinger operator with the Thomas-Fermi potential W

$$A = \Delta + W, \qquad W = V + |x|^{-1} * \rho_{TF}. \tag{8}$$

The physical sense of the second term in W is transparent. Skipping the positive second term in the right-hand expression of (7) and believing that the third term is

[1] Operator with the Schwartz kernel $|x-y|^{-1}$ is positive due to Fefferman-La Llave decomposition for $d \ge 2$.

not very important for the ground state function ψ we see that we need to estimate from below the first term. Here assumption that ψ is antisymmetric is crucial. Namely, for general ψ the best possible estimate is $N\lambda_1$ where λ_1 is the lowest eigenvalue of A (we always assume that there is sufficiently many eigenvalues under the bottom of the essential spectrum of A) and we cannot go further. However, for antisymmetric ψ we get instead

$$\sum_{1\le j\le N} \lambda_j = \mathbf{N}_1(A-\bar\lambda) + \bar\lambda N \tag{9}$$

where $\mathbf{N}(B)$, $\mathbf{N}_1(B)$ are the number and the sum of all the negative eigenvalues of operator B (such that $\mathrm{Spec}_{\mathrm{ess}}(B) \subset \bar{\mathbb{R}}^+$) and $\bar\lambda = \lambda_N < 0$. Applying the semiclassical approximation (need to be justified!) one gets

$$\mathbf{N}_1(A-\bar\lambda) \sim -(2\pi)^{-d}\omega_d d(d+2)^{-1}\int (W-\bar\lambda)_-^{\frac{d+2}{2}}\,dx$$

and therefore the below estimate for the ground state energy is

$$E \ge -(2\pi)^{-d}\omega_d d(d+2)^{-1}\int (W-\lambda)_-^{\frac{d+2}{2}}\,dx + \bar\lambda N - \frac{1}{2}\iint |x-y|^{-1}\rho_{TF}(x)\rho_{TF}(y)dxdy - \text{error}. \tag{10}$$

Furthermore, applying semiclassical approximation for the number $\mathbf{N}(A-\bar\lambda)$ of eigenvalues below $\bar\lambda$ (and this number should be approximately N) one gets an equality

$$N = (2\pi)^{-d}\omega_d \int (W-\bar\lambda)_-^{\frac{d}{2}}dx + \text{error}. \tag{11}$$

On the other hand, let us consider the Euler-Lagrange equation for $\rho = \rho_{TF}$:

$$(1+\frac{2}{d})\varkappa\rho^{\frac{2}{d}} + W = \nu \quad (\rho>0), \qquad W = V + |x|^{-1} * \rho \tag{12}$$

with the Lagrange factor ν. Expressing ρ and integrating we get

$$N = (2\pi)^{-d}\omega_d \int (W-\nu)_-^{\frac{d}{2}}dx. \tag{13}$$

Comparing (11) and (13) we get that with some error $\bar\lambda = \nu$. Substituting to the first term in (10) $\bar\lambda = \nu$ and $\nu - W = \varkappa(1+\frac{d}{2})\rho^{\frac{2}{d}}$ we get the lower estimate $E \ge \mathcal{E}_{TF} - \text{error}$.

To get the upper estimate one takes a test function $\psi(x_1,\dots,x_n)$ which is an antisymmetrization with respect to $(x_1,\dots,x_n)$ of the product $\phi_1(x_1)\cdots\phi_N(x_N)$ where $\phi_1,\dots,\phi_N$ are orthonormal eigenfunctions of A corresponding eigenvalues $\lambda_1,\dots,\lambda_N$. Namely this function minimized the expression

$$\sum_{1\le j\le N} \langle A_{x_j}\psi,\psi\rangle$$

in $\mathcal{H}$. One can write $\psi = \frac{1}{N!}\det\bigl(\phi_i(x_j)\bigr)_{i,j=1,\dots,N}$ and it is called *Slatter determinant*. Obviously, $\|\psi\| = 1$ and $\rho(x) = e_N(x,x)$ where $e_N(x,y) = \sum_j \phi_j(x)\bar{\phi}_j(y)$ is the Schwartz kernel of the projector to the subspace spanned on $\{\phi_j\}_{1\le j\le N}$. Pretty easy calculations show that

$$\langle H\psi,\psi\rangle = \sum_{1\le j\le N}\lambda_j + \frac{1}{2}\iint |x-y|^{-1}(\rho-\rho_{TF})(x)(\rho-\rho_{TF})(y)dxdy- \frac{1}{2}\iint |x-y|^{-1}\rho_{TF}(x)\rho_{TF}(y)dxdy - \frac{1}{2}\iint |x-y|^{-1}|e_N(x,y)|^2dxdy.$$

Let us replace in the first term N by $\mathbf{N}(A-\bar\lambda)$. Then we get $\mathbf{N}_1(A-\bar\lambda)+\bar\lambda\mathbf{N}(A-\mu)$ with an error $\bar\lambda\bigl(N-\mathbf{N}(A-\bar\lambda)\bigr)$ linked with the possible degeneration of the eigenvalue $\bar\lambda = \lambda_N$. Then we get an upper estimate

$$\begin{aligned}(14)\quad E \le{}& \mathbf{N}_1(A-\bar\lambda)+\bar\lambda\mathbf{N}(A-\mu)+\\ &\frac{1}{2}\iint |x-y|^{-1}(\rho-\rho_{TF})(x)(\rho-\rho_{TF})(y)dxdy-\\ &\frac{1}{2}\iint |x-y|^{-1}\rho_{TF}(x)\rho_{TF}(y)dxdy - \frac{1}{2}\iint |x-y|^{-1}|e_N(x,y)|^2dxdy.\end{aligned}$$

Treating the third and fifth terms in the right-hand expression as errors and applying the semiclassical approximation to the first one we get the upper estimate $E \le \mathcal{E}_{TF}+\text{error}$.

So, there are two types of errors. The first is due to replacement E by

$$\mathbf{N}_1(A-\bar\lambda)+\bar\lambda\mathbf{N}(A-\bar\lambda) - \frac{1}{2}\iint |x-y|^{-1}\rho_{TF}(x)\rho_{TF}(y)dxdy$$

and the second is an error of the semiclassical approximation of two first terms including may be the replacement $\bar\lambda$ by ν. Actually, negligence of the third term in (14) is the semiclassical approximation either.

2. Large molecule. I. The most known example is the case of n large nuclei with the charges $Z_1,\dots,Z_n$ located at fixed points $y_1,\dots,y_n$. Then

$$(15)\qquad V(x) = -\sum_{1\le j\le n}\frac{Z_j}{|x-y_j|}$$

in (1). Let us assume that

$$(16)\qquad Z = Z_1+\dots+Z_N = N,\qquad Z_j \ge \epsilon N\quad \forall j(\epsilon>0).$$

The first assumptions means that the system is neutral and it yields that $\nu = 0$. Let us assume that $d = 3$. The properties of ρ_{TF} are well-known. In particular, $\rho_{TF} = N^2\bar\rho(xN^{\frac13})$ where $\bar\rho$ doesn't depend on N explicitly and it is analytic (excluding points $\bar y_j = y_jN^{\frac13}$), positive and vanishing at infinity as $\bigl(\min_j|x-y_j|\bigr)^{-4}$. Then

$$(17)\qquad \mathcal{E}(\rho_{TF}) = \kappa_0 N^{\frac73}$$

with constant $\kappa_0 = \bar{\mathcal{E}} < 0$ (depending on $\bar{y}_j$). It can be proven by the methods of mathematical physics solely that

$$E \ge \mathbf{N}_1(A)|CN^{\frac{5}{3}}. \tag{18}$$

Let us consider operator A. Rescaling as before we get in the new coordinates

$$A = N^{\frac{4}{3}}\bar{A}_h, \qquad \bar{A}_h = h^2\Delta + \bar{W}, \qquad h = N^{-\frac{1}{3}} \tag{19}$$

with potential $\bar{W}$ which doesn't depend on N explicitly. Then $\mathbf{N}_1(A) = N^{\frac{4}{3}}\mathbf{N}_1(\bar{A}_h)$. Weylian semiclassical approximation for $\mathbf{N}_1(\bar{A}_h)$ is $\kappa_0 h^{-3}$ and it yields to approximation $\kappa_0 N^{\frac{7}{3}}$ for E. The error is $O(h^{-2})$ and it yields to the error $O(N^2)$ in the final answer. If potential $\bar{W}$ was smooth the error would be $O(h^{-1})$ for the rescaled one-particle problem and the final error would be $O(N^{\frac{5}{3}})$. However, the Coulomb singularity of $\bar{W}$ at $\bar{y}_j$ produces additional term $\kappa_1 h^{-2}$ with $\kappa_1 = \sum_j z_j^2$, $z_j = Z_j N^{-1}$ in the semiclassical approximation for $\mathbf{N}_1(\bar{A}_h)$ and it yields the *Scott correction term*

$$\sum_j \frac{1}{2} Z_j^2 \tag{20}$$

in the final answer. The error $O(h^{-1})$ (and even $O(h^{\delta-1})$ was recovered in one atom case by Fefferman and Seco (see [FS1,2] for references to earlier papers) and this and all the previous proofs heavily use the spherical symmetry of the problem. Actually, in all these papers variables were separated and the ODE was carefully investigated and the semiclassical approximation for the final answer was obtained by the WKB method. This proof is very sophisticated and very long and it leads to the record-beating estimate but it works only for spherically symmetric system. So, the final error was $O(N^{\frac{5}{3}})$. On the other hand, by methods of the semiclassical spectral asymptotics for PDE Ivrii and Sigal [IS] got an error estimate $O(h^{-\frac{4}{3}})$ for semiclassical approximation (with Scott correction term) for $\mathbf{N}_1(A_h)$ and it leads to the final error $O(N^{\frac{16}{9}})$. Later the error was improved up to $O(h^{-1})$. So, the final error is $O(N^{\frac{5}{3}})$ again. I should note that both results were obtained under (physically reasonable) assumption $|y_j - y_k| \ge \epsilon N^{-\frac{1}{3}} \quad \forall j \ne k$ with an arbitrarily small constant $\epsilon > 0$. It is very important that $\bar{W} - z_j|x - \bar{y}_j|^{-1} = O(1)$ as $x \to y_j$.

However, one can get the remainder estimate $O(N^2)$ without these assumptions. Then applying Tellers lemma one gets immediately that the the excess (ground state energy for molecule with the added potential energy of repulsion between nuclei minus the sum of ground state energies for atoms) is larger than

$$\epsilon_1 N^{\frac{7}{3}}(N^{\frac{1}{3}}\ell + 1)^{-7} - CN^2$$

where ℓ is the minimal distance between nuclei. Here the first term is the lower bound for excess in the Thomas-Fermi approximation and Teller lemma deals with it and second is the remainder estimate. Therefore, assuming that nuclei occupy positions minimizing the ground state energy one gets estimate $\ell \ge N^{-\frac{2}{7}}$. So, our

assumption is justified in this model. Applying now remainder estimate $O(N^{\frac{5}{3}})$ one improves this estimate to $\ell \ge N^{-\frac{5}{21}}$.

The last thing I want to explain is why one can replace $\bar\lambda$ by $\nu = 0$. In the lower it is trivial: $\sum_{\lambda_j \le \bar\lambda} \lambda_j$ doesn't increase if one replaces arbitrary $\bar\lambda$ by 0. In the upper bound one can apply all the above arguments with N replaced by $\bar N = \min(N, \max_{\lambda_j \le 0} j)$ and then one can replace $\bar\lambda = \lambda_{\bar N}$ by 0. Then one gets the proper upper bound for the ground state energy $E(Z, \bar N)$ of the same system but with $\bar N$ electrons. However, according to HVZ-theorem $E(Z, \bar N) \ge E(Z, N)$ if $Z = N \ge \bar N$. I recall that Z is the total charge. Note that these arguments belong to MQT.

3. Large molecule. II. In order to improve the remainder estimate $O(N^{\frac{5}{3}})$ in the final answer one needs to improve the remainder estimate $O(h^{-1})$ in the semiclassical asymptotics for $\mathbf{N}_1(\bar A_h)$ and the remainder estimate in the original reduction.

Let us consider first the semiclassical asymptotics for $\mathbf{N}_1(\bar A_h)$. It is standard that the remainder estimate $O(h^{-1})$ cannot be improved without global assumption: one needs to consider closed Hamiltonian trajectories at the energy level 0 for the corresponding classical Hamiltonian $a(x,\xi) = |\xi|^2 + W(x)$. It is known in the theory of the semiclassical spectral asymptotics and the same conclusion is made in [FS1,2] on the ground of their calculations. So, let us consider $\Sigma = \{(x,\xi), a(x,\xi) = 0\}$ with the natural measure $\mu = dxd\xi : da$ and Hamiltonian flow $\Phi_a(t)$ preserving it. The first very basic conclusion is the following: *if $\mu(P_a) = 0$ where P_a denotes the set of points of Σ, periodic with respect to Φ_a, then*

$$\mathbf{N}_1(\bar A_h) = \kappa_0 h^{-3} + \kappa_1 h^{-2} + \bigl(\kappa_2 + o(1)\bigr) h^{-1} \qquad \text{as } h \to 0 \tag{21}$$

where κ_0, κ_1 are the leading and Scott coefficients and

$$\kappa_2 = \varkappa_1 \int W_-^{\frac{1}{2}} \Delta W dx = -\varkappa_2 \int \rho_{TF}^{\frac{4}{3}} dx. \tag{22}$$

is *Schwinger correction*; $\varkappa_1, \varkappa_2$ are known positive numbers. One can easily justify the basic assumption $\mu(P_a) = 0$ for the atom using the known properties of W. Moreover, one can prove this for molecule as well assuming that $|y_j - y_k| N^{\frac{1}{3}} \to \infty \quad \forall j \ne k$ (physically reasonable assumption). In order to improve this remainder estimate one should assume some properties of the Hamiltonian flow. Namely, to get $O(h^{\delta-1})$ with $\delta > 0$ one should assume no more than power growth of the Jacobian matrix of $\Phi(t)$ and some estimates for the measure of "almost periodic" points. However, for atom it is completely integrable and one can check this properties. For molecule with

$$|y_j - y_k| \ge N^{-\frac{1}{3}+\delta'} \quad \forall j \ne k \tag{22}$$

the necessary properties are due to the properties of atoms (one should take $|t| \le h^{-\delta''}$ with arbitrarily small $\delta'' > 0$. The assumption to the nuclear distances is physically reasonable. So, in the physically interesting case this part of the job is done.

For atoms the arguments of Fefferman-Seco go further: they got the same remainder estimate with the small but *specified* exponent $\delta > 0$. This is the advantage of the explicit calculation over general methods of PDE in the (pretty rare) case when these calculations are possible. Moreover, using the methods of the semiclassical spectral asymptotics one can prove that under assumption (22)

$$\mathbf{N}_1(\bar{A}_h) = \sum_{1\le j\le n} \mathbf{N}_1(\bar{A}_{jh}) + O(h^{-1+\delta})$$

where $\bar{A}_{jh}$ mean reduced "one-atomic" operators and $\delta = 12\delta' - 1$ for $\delta' \le \frac{1}{2}$. Therefore, applying Fefferman-Seco result (asymptotics of $\mathbf{N}_1$) for atom one extends it with the same (pretty small) exponent δ for molecules under this assumption. In the "optimal positions of nuclei model" we already got $\delta' = \frac{2}{21}$ and it is sufficient for this extension. However, I don't know how to extent Fefferman-Seco results for term (25). But it is not necessary, if the lower bound for ℓ (in the original model) is all we want to know. One can now improve it further.

Finally, I would like to notice the following funny result. If *all* the trajectories escape to infinity then the remainder

estimate is linked only with the singularity. Namely, let us assume that $W = f(|x|)$ with $f(r) > 0$, $\partial_r r^2 f(r) > \epsilon_0 r^2 f(r)$, $|\partial_r^\alpha f| \le c r^{-\alpha} f$ for all $\alpha \le K_0$. Further, let us assume that $|\partial^\alpha (W - f_0|x|^{-2q})| \le c|x|^{1-\alpha} f$ for all $\alpha : |\alpha| \le K_0$, $0 < q < 1$. Then one can get the remainder estimate $O(1)$, $O(h^l)$ with $l = (1-2q)(1-q)^{-1}$ for $q \le \frac{1}{2}$, $q > \frac{1}{2}$ respectively. In this case the Scott correction term is $\kappa_1 h^{\bar{l}}$ with $\bar{l} = 2q(q+1)^{-1}$ (with some constant κ_1) and coefficient κ_2 is defined by the different way. Moreover, for $q = \frac{3}{5}$ the first term is $\kappa_0 h^{-3}\log h$ and for $q > \frac{3}{5}$ Scott term is principal and coefficient κ_0 is defined by the different way for $q \ge \frac{3}{5}$. Moreover, this conclusion remains true if $|\partial^\alpha (W - f(|x|)| \le \epsilon |x|^{-\alpha} f$ for all $\alpha : |\alpha| \le 1$ with sufficiently small $\epsilon > 0$.

This is impossible if in the original problem electron-nuclei interaction was Coulombian (because W decays as $|x|^{-4}$. However, I believe that in the case of more slowly decaying at infinity potential V one can get W satisfying these assumptions. However, these funny nuclei can bind an infinite number of electrons.

4. Large molecule. III. Correlations. Only now I pass to the main topic of my talk. Now we need to improve remainder estimate in the reduction. First of all, Graf and Solovej improved the electrostatic inequality and applying it to the problem in question improved the lower estimate:

$$E \ge \mathbf{N}_1(\bar{A}) - \frac{1}{2}\iint |x-y|^{-1}\rho(x)\rho(y)dxdy - \varkappa_3 \int \rho_{TF}^{\frac{4}{3}} dx - O(N^{\frac{5}{3}-\delta}) \tag{23}$$

with some (known) constant $\varkappa_3 > 0$. The one can rewrite the third *(Dirac correction)* term in the form $\varkappa_3 N^{\frac{5}{3}}$. The proof is pretty complicated but completely in frames of MQT (no PDE!). To get an upper estimate we try again the Slater determinant test function. Then we need to consider asymptotics of

$$-\frac{1}{2}\int |\epsilon(x,y)|^2 |x-y|^{-1} dxdy \tag{24}$$

and

$$\frac{1}{2}\int (\rho-\rho_{TF})(x)(\rho-\rho_{TF})(y)|x-y|^{-1}dxdy. \tag{25}$$

Let us start from the first one. We call it *correlation*.

Theorem 1. *In our conditions*

$$\int |e(x,y)|^2|x-y|^{-1}dxdy = 2\varkappa_3\int \bar\rho^{\frac{4}{3}}dxN^{\frac{5}{3}} - O(N^{\frac{4}{3}}). \tag{26}$$

This theorem is a corollary of the following local version and some functional analytical arguments (nevertheless not arguments of mathematical physics):

Theorem 2. *Let us consider Schrödinger operator $A_h = -h^2\Delta + W$. Let A_h be self-adjoint in $L^2(X)$ where X is a domain in $\mathbb{R}^d, d\ge 2$ containing the unit ball $B(0,1)$ and let*

$$|D^\alpha W(x)|\le c \qquad \forall \alpha : |\alpha|\le K. \tag{27}$$

Let $\zeta(x,y)$ be supported in $B(0,\frac{1}{2})\times B(0,\frac{1}{2})$ and

$$|D^{\alpha,\beta}_{x+y,x-y}\zeta|\le c|x-y|^{-p-|\beta|} \qquad \forall \alpha,\beta : |\alpha|+|\beta|\le K \tag{28}$$

with $0<p<d$. Here $K=K(d)$. Then

$$\Big|\int |e(x,y)|^2\zeta(x,y)dxdy - \mathrm{Weyl}\Big|\le Ch^{1-d-p} \tag{29}$$

with

$$\mathrm{Weyl} = (2\pi)^{-2d}\int dx \iiint_{|\xi|^2+W(x)\le 0,|\eta|^2+W(x)\le 0} e^{ih^{-1}\langle z,\xi-\eta\rangle}\zeta(x,z)dzd\xi d\eta$$

where $e(x,y)$ is the Schwartz kernel of the spectral projector $\Pi(0)$. Here $\mathrm{Weyl} = O(h^{-d-p})$ and moreover $\mathrm{Weyl}\asymp h^{-d-p}$ under natural conditions.

The last theorem is due to more general theorem I don't want to discuss here. Moreover, there is no need to improve the remainder estimate for our goal. However, I want to note that the main obstacle are not only closed trajectories but also *loops* (see below).

5. Large molecule. IV. Loops. Let us consider term (25). I recall that $\rho(x)=e(x,x)$. The local theorem is now

Theorem 3. *(i) In frames of theorem 2*

$$\big|\rho(x)-h^{-d}\rho_0(x)\big|\le Ch^{1-d} \qquad \forall x\in B(0,\frac{1}{2}) \tag{30}$$

provided either $d\ge 3$ or

$$W(x)\le -\epsilon \qquad \forall x\in B(0,1): \tag{31}$$

here and below $\rho_0(x) = (2\pi)^{-d}\omega_d W_-^{\frac{d}{2}}$.

(ii) Moreover, for $d = 2$

$$\mathcal{R} = \iint (\rho - h^{-d}\rho_0)(x)(\rho - h^{-d}\rho_0)(y)|x-y|^{-p} \le Ch^{2-2d} \tag{32}$$

$$\mathcal{R}_1 = \int \bigl|(\rho - h^{-d}\rho_0)(x)\bigr|dx \le Ch^{1-d} \tag{33}$$

without condition (31); *I recall* $0 \le p < 2$.

Applying this local theorem one can recover only estimate $O(N^{\frac{5}{3}})$ for (25). In order to improve it one should consider Hamiltonian trajectories. However, at the moment not only closed trajectories seem to cause troubles but loops as well.

Definition 4. Point $(x,\xi) \in \Sigma$ is a loop point if $\Phi_t(x,\xi) = (x,\xi')$ for some $t \ne 0, \xi'$. Note, that $\xi' = \xi$ means exactly that (x,ξ) is periodic.

One can introduce measure $\mu_x = d\mu : d\xi$ on Σ_x, the layer of Σ over x and one can prove easily that left-hand expression in (31) is $o(h^{1-d})$ provided μ_x-measure of the loop points over x is 0 and we can control long-term trajectories. Moreover, if μ-measure of all the loop trajectories is 0 then $\mathcal{R} = o(h^{2-d})$ and $\mathcal{R}_1 = o(h^{1-d})$. *These results with the possible adjustments for well-controlled Hamiltonian flow permit to recover estimate* $o(N^{\frac{5}{3}})$ *and even* $O(N^{\frac{5}{3}-\delta})$ *for* (25) *under condition* (22).

I would like to notice that the μ-measure of the set of loop points which are not periodic is 0 and therefore these points are of the little importance in $\mathcal{R}, \mathcal{R}_1$. Really, due to condition $\xi' \ne \xi$ the loop points form a set of the (natural) measure 0 along any non-periodic trajectory.

6. Jellium model on sphere. To understand the link of the periodic trajectories and (25) let us consider the high-density neutral jellium on the sphere instead of standard $\mathbb{R}^d$. The neutral jellium model means that the potential V is created by the charges uniformly distributed on the manifold X with the density $\bar\rho = N(\operatorname{vol} X)^{-1}$. Then $\rho_{TF}(x) = \bar\rho$ and $W = 0$. So, we get $A = -\Delta$. I will discuss only upper bound. There is a very little doubt that the lower bound can be obtained by Graf-Solovej method. In this case $\lambda = \lambda_N \sim (2\pi)^{\frac{1}{2}}\omega_d^{-\frac{1}{d}}\bar\rho$. In the general model one can get easily upper bound (substituting the Slater determinant as a test function)

$$\mathbf{N}_1(A-\lambda) + \lambda N + \kappa_3 N^{\frac{4}{3}} + \frac{1}{2}\iint (\rho(x)-\bar\rho)(\rho(y)-\bar\rho)|x-y|^{-1}dxdy + O(N) \tag{34}$$

and going to semiclassical expression one gets easily the answer in the form $\kappa_0 N^{\frac{5}{3}} + O(N^{\frac{4}{3}})$ with well-established constants κ_j. Moreover, under condition $\mu(P_a) = 0$ one gets easily the upper bound in the form $\kappa_0 N^{\frac{5}{3}} + \kappa_1 N^{\frac{4}{3}} + o(N^{\frac{4}{3}})$.

Let us consider ultimately $X = \mathbb{S}^d$, $d \ge 2$. There is an explicit formula for $\mathbf{N}_1(A - \lambda_N) + \lambda_N N$ (nevertheless it contains non-Weylian term of the magnitude $N^{\frac{4}{3}}$) and we need to estimate only (25). Note, that nevertheless eigenfunctions corresponding

to eigenvalues less than λ_N are not chosen uniquely, their total contribution to $\rho(x)$ is defined uniquely. However, it is not true for eigenfunctions corresponding to eigenvalue λ_N because only some but not all of them should be taken (the number of these eigenfunctions should be $N - \mathbf{N}(A - \lambda_{N-1})$. This arbitrary choice doesn't affect other terms in (34). One can note easily that (25) doesn't change if one takes $\rho(x)$ corresponding only to these last M eigenfunctions and $\bar{\rho} = (\operatorname{vol} X)^{-1} M$. Let $M_N \asymp N^{1-\frac{1}{d}}$ be the dimension of the eigenspace corresponding to λ_N; formula is known but out of importance. It is not true that for any N and $M = 1, \dots, M_N$ one can pick eigenfunctions with $\rho(x) = \bar{\rho}$. However, $|\rho(x) - \bar{\rho}| \le C M_N$ for any choice of these eigenfunctions and $\operatorname{mes}\{x, |\rho(x) - \bar{\rho}| \ge \epsilon M_N\} \le \varepsilon(N, \epsilon)\}$ for an appropriate choice of these eigenfunctions where $\epsilon > 0$ is arbitrarily small and $\varepsilon(N, \epsilon) \to 0$ as $N \to \infty$. Thus, *upper estimate*

$$\mathbf{N}_1(A - \lambda) + \lambda N + \kappa_3 N^{\frac{4}{3}} + o\big(N^{\frac{4}{3}}\big)$$

holds and I am sure that one can replace $o\big(N^{\frac{4}{3}}\big)$ by $O\big(N^{\frac{4}{3}-\delta}\big)$ using the same arguments.

Moreover, it is not very difficult to treat jellium model for manifold X with the boundary and even with singularities of some type.

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