On semiclassical limiting eigenvalue distribution theorems for the hydrogen atom in a weak and constant magnetic field.

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Limiting eigenvalue distribution theorem for the n-sphere. A. Weinstein, 1977.

Let $S^n = \{x \in \mathbb{R}^{n+1} \mid |x| = 1\}$ be the n-sphere , $n \geq 2$.
Let Δ_{S^n} be the Laplacian on S^n.

The spectrum of Δ_{S^n} consists of discrete eigenvalues
$\lambda_\ell = \left(\ell + \frac{n-1}{2}\right)^2$ with multiplicity $d_\ell = O(\ell^{n-1})$, $\ell = 0, 1, \ldots$

Let $V : S^n \to \mathbb{R}$ be a continuous potential.
Consider the Schrödinger operator $H = \Delta_{S^n} + V$ densely defined on $L^2(S^n)$.

The spectrum of H is discrete and, sufficiently far form the origin, consists of clusters of eigenvalues of size no larger than $\|V\|_\infty$ around λ_ℓ. Each cluster has as many as d_ℓ eigenvalues counting multiplicity.

Notation: For ℓ fixed and sufficiently large, denote the eigenvalues of H within the ℓth cluster by $\lambda_{\ell,m}$, $m = 1, 2, \ldots, d_\ell$.

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Theorem (A. Weinstein)

Let $F \in C_0^\infty(\mathbb{R})$ and $V : S^n \to \mathbb{R}$ continuous. Then

$$\lim_{\ell\to\infty} \frac{1}{d_\ell} \sum_{m=0}^{d_\ell} F(\lambda_{\ell,m} - \lambda_\ell) = \int_{\gamma\in\Gamma} F(\hat{V}(\gamma)) d\nu(\gamma)$$

with Γ = space of oriented geodesics of S^n, and $\hat{V} : \Gamma \to \mathbb{R}$ the Radon transform of V.

$\hat{V} : \Gamma \to \mathbb{R}$ given by

$$\hat{V}(\gamma) = \frac{1}{2\pi} \int_0^{2\pi} V(\gamma(s)) ds, \quad \gamma \in \Gamma.$$

with $\gamma(s)$ a parametrization of γ with respect to arc length s.

$d\nu$ is the SO(n+1)-invariant normalized measure on Γ.

Note the appearence of the classical Hamiltonian flow (the geodesic flow in this case) corresponding to the quantum unperturbed problem (the Laplacian on S^n).

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Other ways to state Weinstein theorem:

For ℓ sufficiently large, consider the Riesz projector P_ℓ associated to the cluster of eigenvalues of H around λ_ℓ.

Then

$$\lim_{\ell\to\infty} \frac{1}{d_\ell} tr\left[\, F\left(P_\ell\left(H-\lambda_\ell\right)P_\ell\right)\,\right] = \int_{\gamma\in\Gamma} F(\hat{V}(\gamma))d\nu(\gamma)$$

The above equation has the following spirit:

$$\text{(quantum mechanics and functional analysis)} \xrightarrow{\ell\to\infty} \text{(classical mechanics and symplectic geometry)}$$

Let $d\mu_V$ be the measure on the real line given by $d\mu_V = \hat{V}_*(d\nu)$.

Note that $d\mu_V$ can be thought of as both the measure determined by a Riesz representation theorem and the weak limite measure of the sequence of measures $d\mu_\ell = \frac{1}{d_\ell}\sum_{m=0}^{d_\ell} \delta_{\lambda_{\ell,m}-\lambda_\ell}$. Thus

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Hydrogen atom Hamiltonian:
$S_{V,\hbar} = -\frac{\hbar^2}{2}\Delta_{\mathbb{R}^n} - \frac{1}{|\mathbf{x}|}, \quad L^2(\mathbb{R}^n), n \geq 2$
Eigenvalues: $E_\ell^{(\hbar)} = -\frac{1}{2\hbar^2\left(\frac{n-1}{2}+\ell\right)^2}$, multiplicity$=d_\ell = O(\ell^{n-1})$,
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Let N be a positive integer number. Regard $\hbar(N) = \frac{1}{\frac{n-1}{2}+N}$.

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$E_N^{(\hbar(N))} = -\frac{1}{2}$ is an eigenvalue of $S_{V,\hbar(N)}$ for all N with multiplicity $d_N = O(N^{n-1})$.

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Let $Q : L^2(\mathbb{R}^n) \mapsto L^2(\mathbb{R}^n)$ be a continuous bounded function.

Consider the operators $H_\hbar = -\frac{\hbar^2}{2}\Delta_{\mathbb{R}^n} - \frac{1}{|\mathbf{x}|} + \epsilon(\hbar)Q$ with $\epsilon(\hbar) = O(\hbar^{1+\delta}), \quad \delta > 0$ and $\hbar(N) = \frac{1}{\frac{n-1}{2}+N}$ as above.

$H_{\hbar(N)}$ has a cluster of $d_N = O(N^{n-1})$ eigenvalues around $-1/2$.

Let us denote by $\lambda_{N,j} = -\frac{1}{2} + \mu_{N,j}, \quad j = 1, \ldots, d_N,$ the eigenvalues in that cluster around $-1/2$.

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Theorem (Uribe, Villegas-Blas, 2008)

Let Q_h be a pseudodifferential operator of order zero with principal symbol a_0 in the class $S_{2n}(1)$ so that $\|Q_h\|$ is bounded uniformly with respect to $\hbar$. Then for F continuous on the real line,

$$\lim_{N\to\infty} \frac{1}{d_N} \sum_{j=1}^{d_N} F\Big(\frac{\mu_{N,j}}{\epsilon(\hbar)}\Big) = \int_{\Sigma(-1/2)} F\left(\frac{1}{2\pi}\int_0^{2\pi} a_0(\tilde{\phi}_t(x,p))\,dt\right)\,d\mu_L(x,p)$$

where $\tilde{\phi}_t$ denotes the Hamiltonian flow of the Kepler problem on the surface $\Sigma(-1/2) = \{(\mathbf{x},\mathbf{p}) \mid \frac{|\mathbf{p}|^2}{2} - \frac{1}{|\mathbf{x}|} = -\frac{1}{2}\}$ and $d\mu_L$ the normalized Liouville measure on $\Sigma(-1/2)$.

- Collision orbits are included. Moser regularization (1970). Geodesic flow $\Leftrightarrow$ Kepler problem, energy $-1/2$. Time reg.
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Hydrogen atom ($n=3$) in a constant magnetic field $\epsilon(\hbar)\overrightarrow{B}$, $\overrightarrow{B}=(0,0,B)$. Zeeman effect.

Coulomb potential $V(\mathbf{x}) = -\frac{1}{|\mathbf{x}|}$.

The **Zeeman hydrogen Hamiltonian is**

$$H_V(\hbar,B) : \mathcal{D}om(H_V(\hbar,B)) \subset L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3),$$

$$\begin{aligned} H_V(\hbar,B) &= \frac{1}{2}\left(-i\hbar\nabla - \epsilon(\hbar)\overrightarrow{A}\right)^2 - \frac{1}{|x|} \\ &= S_{V,\hbar} + w(\hbar,B). \end{aligned}$$

where $\overrightarrow{A} = (B/2)(-x_2, x_1, 0)$, $\overrightarrow{B} = \nabla \times \overrightarrow{A}$, $S_{V,\hbar} = -\frac{\hbar^2}{2}\Delta_{\mathbb{R}^n} - \frac{1}{|\mathbf{x}|}$ and the **Zeeman perturbation** $w(\hbar,B)$ is given by

$$w(h,B) = \frac{(\epsilon(\hbar)B)^2}{8}(x_1^2+x_2^2) - \frac{\epsilon(\hbar)B}{2}\hbar L_3,$$

with $L_3 = -\imath\left(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1}\right)$.

Hydrogen atom ($n = 3$) in a constant magnetic field $\epsilon(\hbar)\overrightarrow{B}$, $\overrightarrow{B} = (0, 0, B)$. Zeeman effect.
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Based on a stability theorem due to Avron, Herbst, Simon, we can show that under the perturbation $\epsilon(h)\overrightarrow{B}$, the eigenvalue $E = -1/2$ gives rise to a cluster of nearby eigenvalues $E_{N,j}, j = 1, \ldots, d_N$.

Theorem (Avendaño, Hislop, Villegas-Blas)

Let $B > 0$ be fixed, and let F be a continuous function on $\mathbb{R}$. Let $\epsilon(h) = h^{33/2+\delta}$, for some $\delta > 0$, and take $h = 1/(N+1)$, with $N \in \mathbb{N}$. For the eigenvalue cluster $\{E_{N,j}\}$ near $-1/2$, we have

$$\lim_{N\to\infty} \frac{1}{d_N} \sum_{j=1}^{d_N} F\left(\frac{E_{N,j} - (-1/2)}{\epsilon(1/(N+1))}\right) =$$

$$\int_{\Sigma(-1/2)} F\left(-\frac{B}{2} L_3(x,p)\right) d\mu_L(x,p) = \int_{-1}^{1} F\left(\frac{-B}{2} u\right)(1 - |u|)\, du$$

where $L_3(x,p) = x_1 p_2 - x_2 p_1$ is the third component of the classical angular momentum on the energy surface $\Sigma(-1/2)$ with collision orbits included. μ_L is the normalized Liouville measure on $\Sigma(-1/2)$. du is the Lebesgue measure on $[-1,1]$.

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For $\epsilon(\hbar) = \hbar^q$, $q > 19$, and N sufficiently large, we have that, inside the corresponding cluster around $-1/2$, the spectrum of the operator $H_{\hbar(N)}$ is contained in the disjoint union of the intervals

$$[-\frac{1}{2}-\frac{B}{2}\frac{m}{N+1}\epsilon(\hbar)-\epsilon(\hbar)O(N^{-\sigma}), -\frac{1}{2}-\frac{B}{2}\frac{m}{N+1}\epsilon(\hbar)-\epsilon(\hbar)O(N^{-\sigma})]$$

with $\sigma > 1$ and $m = -N, \ldots, N$.

Moreover, the multiplicity in each one of those intervals is $N + 1 - |m|$ respectively, i. e . we have sub-clusters denoted by $\mathcal{C}_{N,m}$. Let us denote the eigenvalues of $H_{\hbar(N)}$ inside the sub-cluster $\mathcal{C}_{N,m}$ by $E_{N,m,k}$ with $k = 1, \ldots, N + 1 - |m|$.

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Let $\mu = \frac{m}{N+1}$ fixed. We have the following

Theorem (Avendaño, Hislop, Villegas-Blas)

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$$\lim_{N\to\infty} \frac{1}{N+1-|m|} \sum_{k=1}^{N+1-|m|} F\left(\frac{E_{N,\mu N+1,k} - \left(-\frac{1}{2} - \frac{B}{2}\mu\epsilon(\hbar)\right)}{\epsilon^2(1/(N+1))} \right) =$$

$$\int_{\Sigma(-1/2,\mu)} F\left(\frac{B^2}{8} \frac{1}{2\pi} \int_0^{2\pi} a_0(\tilde{\phi}_t\,(x,p)) \right) d\mu_{L,\mu}(x,p)$$

where $\Sigma(-1/2,\mu)$ denotes the set of points $(x,p) \in \mathbb{R}^6$ with energy $E = -1/2$ and $L_3(x,p) = \mu$. The function $a_0 : \mathbb{R}^6 \mapsto \mathbb{R}$ is given by $a_0(x,p) = x_1^2 + x_2^2$. The measure $\mu_{L,\mu}$ is the restriction of the Liouville measure μ_L to the set $\Sigma(-1/2,\mu)$.

Dilation operator. For $r > 0$, $D_r : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$, $D_r \Psi(\mathbf{x}) = r^{3/2}\Psi(r\mathbf{x})$. Consider the following re-scaling:

$$D_{\hbar^2} H_V(\hbar, B) D_{\hbar^{-2}} = \frac{1}{h^2} S_V(\lambda(h, B))$$

where the **scaled Zeeman hydrogen hamiltonian** $S_V(\lambda(h, B))$ is defined via the **effective magnetic field** $\lambda(h, B) = h^3 \epsilon(h) B$ and the operator $S_V(\lambda)$ given by:

$$\begin{aligned} S_V(\lambda) &= -\frac{1}{2}\Delta - \frac{1}{|x|} + \frac{\lambda^2}{8}(x_1^2 + x_2^2) - \frac{\lambda}{2} L_3 \\ &= S_V + W(\lambda). \end{aligned}$$

where we write $S_V \equiv -\frac{1}{2}\Delta - \frac{1}{|x|}$ for the scaled hydrogen atom Hamiltonian and

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Four operators:

$$S_0 = -\frac{1}{2}\Delta$$
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Spectrum:

$$\sigma(S_0) = [0, \infty)$$
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Avron, Herbst, Simon show we do not have

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Lemma (Key Lemma)

Consider $\mathbf{z}\notin[0,\infty)$.

(i) *We have the following norm convergence :*

$$V(S_0(\lambda)-\mathbf{z})^{-1}\to V(S_0-\mathbf{z})^{-1},\qquad \lambda\to 0.$$

(ii) *Consider* $\lambda=\lambda(\hbar)$ *with* $\hbar=1/(N+1)$ *and* $\epsilon(\hbar)=\hbar^q$, $q>3/2$. *For* $|\mathbf{z}-E_N|=O(N^{-3})$ *we have*

$$V(S_0(\lambda(\hbar))-\mathbf{z})^{-1}-V(S_0-\mathbf{z})^{-1}=O\left(N^{-\left(\frac{2}{5}q-\frac{3}{5}\right)}\right),\qquad N\to\infty$$

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Theorem (Stability theorem)

Given $B > 0$ and $q > 9$, the following spectral projectors are well defined for N sufficiently large and $\hbar = 1/(N+1)$:

$$P_N = -\frac{1}{2\pi\imath}\int_{\Gamma_N} (S_V(\lambda(\hbar, B)) - \mathbf{z})^{-1}\, d\mathbf{z}$$

$$\Pi_N = -\frac{1}{2\pi\imath}\int_{\Gamma_N} (S_V - \mathbf{z})^{-1}\, d\mathbf{z}.$$

Moreover

$$\|P_N - \Pi_N\| = O(N^{-\frac{2q-33}{5}})$$

so that, for $q > 33/2$, the spectrum of $S_V(\lambda(h = 1/(N+1), B))$ inside the circle Γ_N consist of a cluster of d_N eigenvalues taking N sufficiently large.

On the size of the eigenvalue cluster around $E_N = \frac{-1}{2(N+1)^2}$.

Let us denote by $\tilde{E}_{N,j}$, $j = 1, \ldots, d_N$, the eigenvalues of $S_V(\lambda)$ inside the circle Γ_N (this notion is well defined for N large). Now we consider the eigenvalue shifts $\tilde{\nu}_{N,j} = \tilde{E}_{N,j} - E_N$ thinking of them as the eigenvalues of the operator $P_N(S_V(\lambda) - E_N)P_N$. Taking $q > 33/2$, we have for $\sigma = \frac{2q-33}{5} > 0$,

$$\begin{aligned} P_N(S_V(\lambda) - E_N)P_N &= \Pi_N W(\lambda)\Pi_N + (P_N - \Pi_N)\,W(\lambda)\Pi_N \\ &\quad + P_N W(\lambda)\Pi_N \left\{ [I - (P_N - \Pi_N)]^{-1} - I \right\} \\ &= \Pi_N W(\lambda)\Pi_N + O(N^{-\sigma})W(\lambda)\Pi_N \\ &\quad + P_N W(\lambda)\Pi_N O(N^{-\sigma}) \end{aligned}$$

We have $\|L_3\Pi_N\| = \|\Pi_N L_3 \Pi_N\| = O(N)$ and using coherent states we can also show $\|\left(x_1^2 + x_2^2\right)\Pi_N\| = O(N^4)$ which implies $\|W(\lambda)\Pi_N\| = O\left(h^2\epsilon(h)\right)$. Thus we conclude

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Theorem

Let F be a continuous function on $\mathbb{R}$. Then for $\hbar = 1/(N+1)$ and $q > 33/2$,

$$\frac{1}{d_N}\sum_{j=1}^{d_N} F\left(\frac{E_{N,j} - (-1/2)}{\epsilon(1/(N+1))}\right) = \frac{1}{d_N}\mathrm{Tr}\, F\left(\Pi_N\left(-\frac{B}{2}\hbar L_3\right)\Pi_N\right) + O(N^{-\sigma}).$$

Remark: It is enough to show the theorem when F is actually a monomial. Note that L_3 commutes with Π_N.

The Fock transform.

Inverse of the stereographic projection $S : \mathbb{R}^n \mapsto S_o^n$,

$$\omega_i = \frac{2p_i}{|\mathbf{p}|^2+1}, \quad i = 1, \ldots, n \qquad \omega_{n+1} = \frac{|\mathbf{p}|^2-1}{|\mathbf{p}|^2+1}.$$

$K : L^2(S^n) \mapsto L^2(\mathbb{R}^n)$

$$\forall f \in L^2(S^n) \qquad K(f)(\mathbf{p}) = \left(\frac{2}{|\mathbf{p}|^2+1}\right)^{n/2} f(S(\mathbf{p})).$$

$J : L^2(\mathbb{R}^n) \mapsto L^2(\mathbb{R}^n)$

$$J(\hat{\Psi})(\mathbf{p}) = \frac{2}{|\mathbf{p}|^2+1}\hat{\Psi}(\mathbf{p}).$$

Denote by $\mathcal{E}_N$ the eigenspace of $A = -\frac{1}{2}\Delta_{\mathbb{R}^n} - \frac{1}{|\mathbf{x}|}$ with eigenvalue $E_N = -\frac{1}{2(N+\frac{n-1}{2})^2}$. Then the operator

$$\begin{array}{rcl} \mathcal{F}(\mathcal{E}_N) & \rightarrow & L^2(S^n) \\ \hat{\Psi} & \mapsto & K^{-1}J^{-1/2}D_{r_N^{-1}}(\hat{\Psi}), \end{array}$$

where $r_N = N + (n-1)/2$, is a unitary isomorphism onto V_N.

THE NULL QUADRIC.

Given n a positive integer number, we define the null quadric by

$$Q^n = \{\boldsymbol{\alpha} \in \mathbb{C}^{n+1} | \alpha_1^2 + \ldots + \alpha_{n+1}^2 = 0\}$$

$$\boldsymbol{\alpha} \in Q^n \quad \text{iff} \quad |\Re\boldsymbol{\alpha}| = |\Im\boldsymbol{\alpha}| \quad \text{and} \quad \Re\boldsymbol{\alpha} \cdot \Im\boldsymbol{\alpha} = 0$$

$$\sigma : Q^n - \{0\} \longmapsto T^*S^n - \{0\},$$
$$\sigma(\boldsymbol{\alpha}) = \left(\frac{\Re\boldsymbol{\alpha}}{|\Re\boldsymbol{\alpha}|}, -\Im\boldsymbol{\alpha} \right)$$

$$\mathcal{A} = \{\boldsymbol{\alpha} \in Q^n \mid |\Re\boldsymbol{\alpha}| = |\Im\boldsymbol{\alpha}| = 1\}$$

Coherent states on the n-sphere

$$\Phi_{\boldsymbol{\alpha},\ell}(\mathbf{w}) \equiv a(\ell)\,(\boldsymbol{\alpha}\cdot\mathbf{w})^{\ell}, \quad \mathbf{w}\in S^n, \quad \boldsymbol{\alpha}\in\mathcal{A}.$$

with $a(\ell)$ a normalization constant.

Properties:

- $\Delta_{S^n}\Phi_{\boldsymbol{\alpha},\ell} = \lambda_\ell \Phi_{\boldsymbol{\alpha},\ell} \;\; , \quad \Phi_{\boldsymbol{\alpha},\ell}\in V_\ell.$
- Resolution of the identity: For all $f\in V_\ell$,

$$\begin{aligned} f &= d_\ell \int_{\boldsymbol{\alpha}\in\mathcal{A}} < \Phi_{\boldsymbol{\alpha},\ell}, f > \Phi_{\boldsymbol{\alpha},\ell}\, d\mu(\boldsymbol{\alpha}), \\ \Pi_\ell &= d_\ell \int_{\boldsymbol{\alpha}\in\mathcal{A}} |\Phi_{\boldsymbol{\alpha},\ell} >< \Phi_{\boldsymbol{\alpha},\ell}|\, d\mu(\boldsymbol{\alpha}). \end{aligned}$$

- For $T: L^2(S^n)\mapsto L^2(S^n)$ a bounded operator,

$$tr\,(\Pi_\ell T \Pi_\ell) = d_\ell \int_{\boldsymbol{\alpha}\in\mathcal{A}} < \Phi_{\boldsymbol{\alpha},\ell}|T|\Phi_{\boldsymbol{\alpha},\ell} > d\mu(\boldsymbol{\alpha})$$

- Concentration for ℓ large on the great circle generated by $\Re\boldsymbol{\alpha}$ and $\Im\boldsymbol{\alpha}$.

Coherent states for the hydrogen atom: $\Psi_{\boldsymbol{\alpha},\ell} = \mathcal{F}^{-1}\hat{\Phi}_{\boldsymbol{\alpha},\ell}$
with $\hat{\Phi}_{\boldsymbol{\alpha},\ell} = U^{-1}\Phi_{\boldsymbol{\alpha},\ell}$
Key Lemma:

Lemma

There exist $r_0 > 0$ independent of $\boldsymbol{\alpha}$ and N such that for all non-negative integer numbers p and s

$$\lim_{N\to\infty} N^s \int_{|\mathbf{x}|\geq r_0} |\mathbf{x}|^p |D_{(N+1)^2}\Psi_{\boldsymbol{\alpha},\ell}|^2 d\mathbf{x} = 0$$

Lemma

Let Π_N be the projector to the eigenspace associated to the eigenvalue E_N of the scaled hydrogen atom hamiltonian S_V as above. Then for $N \to \infty$ and $k \in \mathbb{N}$ fixed we have

$$\begin{aligned} \Pi_N L_3 \Pi_N &= O(N), \\ \Pi_N (x_1^2 + x_2^2)^k \Pi_N &= O(N^{4k}). \end{aligned}$$

Lemma

For $\alpha \in \mathcal{A}$, m a non-negative integer number and $h = 1/(N+1)$, we have for $N \to \infty$

$$\langle \Psi_{\alpha,N}, (hBL_3)^m \, \Psi_{\alpha,N} \rangle = (BL_3(\alpha))^m + O(N^{-1})$$

where $L_3(\alpha) = \Re(\alpha)_1 \Im(\alpha)_2 - \Re(\alpha)_2 \Im(\alpha)_1$ is the angular momentum in the third direction associated to the point $(x,p) = \mathcal{M}^{-1}(\alpha)$ where $\mathcal{M}$ is the inverse of the Moser map $\mathcal{M} : T^*(\mathbb{R}^n) \to T^*(\mathbb{S}^3)$ and α is regarded as an element of $T_1^*(\mathbb{S}^3)$.

Theorem

Let $F : \mathbb{R} \to \mathbb{R}$ *be continuous. Then, we have*

$$\lim_{N\to\infty} \frac{1}{d_N} Tr\left(F\left(\Pi_N \left(-\frac{B}{2} h L_3 \right) \Pi_N \right)\right) = \int_{\Sigma(-1/2)} F\left(-\frac{B}{2} L_3(x,p) \right) \, d\mu_L(x,p)$$

where $L_3(x,p) = x_1 p_2 - x_2 p_1$ is the classical angular momentum.

Existence of suclusters fixing an eigenvalue of the angular momentum operator L_z. Work by M. Karasev (reduction of coherent states). Averaging Method.

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