SEMICLASSICAL SZEGÖ LIMIT OF RESONANCE CLUSTERS FOR THE HYDROGEN ATOM STARK HAMILTONIAN

PETER D. HISLOP AND CARLOS VILLEGAS-BLAS

Abstract. We study the weighted averages of resonance clusters for the hydrogen atom with a Stark electric field in the weak field limit. We prove a semiclassical Szegö-type theorem for resonance clusters showing that the limiting distribution of the resonance shifts concentrates on the classical energy surface corresponding to a rescaled eigenvalue of the hydrogen atom Hamiltonian. This result extends Szegö-type results on eigenvalue clusters to resonance clusters. There are two new features in this work: first, the study of resonance clusters requires the use of non self-adjoint operators, and second, the Stark perturbation is unbounded so control of the perturbation is achieved using localization properties of coherent states corresponding to hydrogen atom eigenvalues.

Contents

1. Introduction: Semiclassical Szegö limits

The behavior of eigenvalue clusters resulting from the perturbation of highly degenerate eigenvalues of elliptic operators on compact manifolds has been studied by many researchers, notably by V. Guillemin [3] and by A. Weinstein [9]. The basic idea is the following. Suppose that E_N is an eigenvalue of an elliptic self-adjoint operator P with multiplicity d_N, growing with N. For bounded perturbations Q_N, satisfying $\|Q_N\| \to 0$ as $N \to \infty$, there is a cluster of nearby eigenvalues $E_{N,j}$, with the same total multiplicity d_N as E_N, that tend to E_N as $N \to \infty$. The eigenvalue shifts $\nu_{N,j}$ are defined by $\nu_{N,j} \equiv E_N - E_{N,j}$. The basic question concerns the distribution of these eigenvalue shifts as $N \to \infty$. Since the eigenvalue E_N is increasing with N, the Hamiltonian is rescaled so that the eigenvalue $\tilde{E}$ is independent of N. This rescaling results in a rescaled perturbation and rescaled eigenvalue shifts $\tilde{\nu}_{N,j}$. If the rescaled perturbation $\tilde{Q}_N$ vanishes with a rate $\kappa(N)$, then the rescaled eigenvalue shifts $\tilde{\nu}_{N,j}$ vanish at the same rate. Consequently, the point measure $(1/d_N)\sum_{j=1}^{d_N} \delta(\lambda - \tilde{\nu}_{N,j}/\kappa(N))d\lambda$ should have a weak limit as $N \to \infty$. In particular, if $\rho \in C_0(\mathbb{R})$, then, roughly speaking, one proves that

$$\lim_{N\to\infty} \frac{1}{d_N} \sum_{j=1}^{d_N} \rho\left(\frac{\tilde{\nu}_{N,j}}{\kappa(N)}\right) = \int_{\mathcal{A}} \rho(\tilde{Q}(\alpha))\; d\mu(\alpha), \tag{1}$$

where $\mathcal{A}$ is a parameterization of the classical Hamiltonian orbits with energy $\tilde{E}$ and μ is an invariant measure on this energy surface. The effective potential $\tilde{Q}$ is the average of a re-scaled perturbation over one of these orbits.

In the semiclassical context, we interpret $h = 1/N$ as Planck's constant, and then this formula (1) is what we mean by a *semiclassical Szegö limit* for the appropriately rescaled eigenvalue shifts of perturbed operator. Formula (1) expresses the weak limit of the distribution function of the eigenvalue shifts in terms of averages of the perturbation over corresponding classical orbits.

The behavior of eigenvalue clusters for bounded perturbations V of the Laplacian $-\Delta_{\mathbb{S}^n}$ on $L^2(\mathbb{S}^n)$ were studied by Guillemin [3]. Weinstein [9] studied these Szegö-type limits for the Laplacian on a compact manifold perturbed by a bounded, real-valued function V. In both cases, the semiclassical parameter is the index of the unperturbed eigenvalue. The integral on the right in (1) is the average of potential perturbation V over closed geodesics of the manifold. Brummelhuis and Uribe [2] extended these results to the study of the semiclassical Schrödinger operator $-h^2\Delta + V$ on $L^2(\mathbb{R}^n)$. The potential $V \geq 0$ is smooth with $V_\infty \equiv \liminf_{|x|\to\infty} V(x) > 0$. They studied the semiclassical behavior of the eigenvalue cluster near an energy $0 < E^2 < V_\infty$. They proved an asymptotic expansion of $Tr\rho[(H_h^{1/2} - E)h^{-1}]$ as $h \to 0$ and related the coefficients to the classical flow for $p^2 + V$ on the energy surface E.

Uribe and Villegas-Blas [8] extended these results by considering perturbations of the hydrogen atom Hamiltonian by operators of the form $\epsilon(h)Q_h$ where Q_h is a zero-order pseudo-differential operator uniformly bounded in h and $\epsilon(h) = \mathcal{O}(h^{1+\delta})$, for $\delta > 0$. The main novelty comes from the fact that for a fixed negative energy, there are two types of classical orbits for the Hamiltonian flow on an energy surface for negative energy. There are bounded periodic orbits corresponding to nonzero angular momentum, and there are unbounded collision orbits with zero angular momentum. Uribe-Villegas [8] used Moser's regularization of collision orbits so that all orbits are considered periodic orbits. In this regularization, all orbits correspond to geodesics on the sphere $\mathbb{S}^3$. Those passing through the north pole are the collision orbits. The geodesics on $\mathbb{S}^3$ are parameterized by a certain five-dimensional set $\mathcal{A}$ described in Appendix 1, section 6.

In this paper, we extend these results to resonances of the Stark hydrogen Hamiltonian. We prove a Szegö-type result on the semiclassical behavior of the distribution of the resonance shifts. To explain this in more detail, let $E_N(h) = -1/(2h^2N^2)$ be an eigenvalue of the hydrogen atom Hamiltonian $H_V(h) = -(1/2)h^2\Delta - |x|^{-1}$, defined on $L^2(\mathbb{R}^3)$ (see (3)), with multiplicity $d_N = N^2$. Applying an external electric field of strength $F > 0$, the resulting Hamiltonian $H_V(h, F) = H_V(h) + F\epsilon(h)x_1$, called here the *Stark hydrogen atom Hamiltonian* (see (5)), has purely absolutely continuous spectrum equal to the real line $\mathbb{R}$. We will keep $F > 0$ constant assume that $\epsilon(h)$ vanishes as $h \to 0$ corresponding to weak field limit. Under the perturbation by the electric field, the eigenvalue $E_N(h) < 0$ gives rise to a cluster of nearby resonances $z_{N,i}(h, F), i = 1, \dots, K_N$, with total algebraic multiplicity equal to d_N. We have $\Re z_{N,i}(h, F) \sim E_N(h)$ and the imaginary part of the resonance $\Im z_{N,i}(h, F)$ is exponentially small in $1/(hF)$.

To study the semiclassical limit, we take $h = 1/N$ as in Uribe-Villegas [8]. Then, the family of hydrogen atom Hamiltonians $H_V(1/N, F = 0)$ has a fixed eigenvalue $E_N(1/N) = -1/2$. The Stark hydrogen atom Hamiltonian $H_V(1/N, F)$ has a cluster of nearby resonances $z_{N,i}(1/N, F)$ that converge to $-1/2$ as $N \to \infty$. Our main result is the following Szegö-type theorem for this resonance cluster in the large N limit corresponding to a weak electric field.

Theorem 1. *Let $F > 0$ be fixed, and let ρ be a function analytic in a disk of radius $3F$ about $z = 0$. Let $\epsilon(h) = h^{6+\delta}$, for some $\delta > 0$, small, and take $h = 1/N$, with $N \in \mathbb{N}$. For the resonance cluster $\{z_{N,i}(1/N, F)\}$ near $E_N(1/N) = -1/2$, we have*

$$\begin{aligned} \lim_{N\to\infty} \frac{1}{d_N} \sum_{j=1}^{d_N} \rho\left(\frac{z_{N,i}(1/N, F) - E_N(1/N)}{\epsilon(1/N)}\right) \\ = \int_{\Sigma(-1/2)} \rho\left(\frac{1}{2\pi}\int_0^{2\pi} F \cdot (\tilde{\phi}_t(x,p))_1 \, dt\right) \, d\mu_L(x,p), \end{aligned} \tag{2}$$

where $\tilde{\phi}_t$ is the Hamiltonian flow for the Kepler problem on the energy surface $\Sigma(-1/2)$ with collision orbits treated as in [8]*, and $\tilde{\phi}_t(x(t), p(t)))_1$ is the projection of this flow onto the first coordinate axis x_1. The measure μ_L is the normalized Liouville measure on restricted to the energy surface $\Sigma(-1/2)$.*

This result parallels and extends the result of Uribe and Villegas-Blas [8] on eigenvalue clusters formed by bounded perturbations Q_h of the hydrogen atom Hamiltonian. There are three new main components in this work. The first is that the Stark perturbation is unbounded. The bounded perturbation Q_h of Uribe-Villegas [8] is replaced by the unbounded perturbation $F\epsilon(h)x_1$ with small field strength as $h \to 0$. Control of the unbounded perturbation is obtained by utilizing the localization properties of coherent states of the hydrogen atom Hamiltonian. The second is the fact that we work with resonances that appear as eigenvalues of non self-adjoint operators. Consequently, many estimates appearing in [8] have to be established for non self-adjoint operators. Thirdly, we use a semiclassical result of Thomas-Villegas [7, Theorem 4.2] to evaluate the trace of the Stark perturbation restricted to certain finite-dimensional subspaces (see Theorem 5.)

1.1. **Contents.** In section 2, we rescale the Stark hydrogen atom Hamiltonian using the dilation group. This establishes a countable family of rescaled Hamiltonians all having a fixed eigenvalue $-1/2$. In section 3, we review the results of Herbst [4] on resonances for the Stark hydrogen atom Hamiltonian. We prove several important resolvent estimates necessary for our work, extending some estimates of Herbst [4]. The main semiclassical result is proved in section 4. We show that the semiclassical Szegö-type limit can be obtained by evaluating the trace of the Stark perturbation restricted to the eigenspace of the hydrogen atom Hamiltonian. This requires decay properties of the analytically continued coherent states. The final part of the proof of Theorem 1 is proved in section 5. We apply a theorem of Thomas-Villegas [7] to polynomially bounded perturbations in order to evaluate the large N limit of the trace of the Stark perturbation restricted to the hydrogen atom Hamiltonian eigenspace.

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2. Scaling

The hydrogen atom Hamiltonian $H_V(h)$ with the semiclassical parameter h acts on the Hilbert space $L^2(\mathbb{R}^3)$. It is the self-adjoint operator given by

$$H_V(h) = -\frac{h^2}{2}\Delta - \frac{1}{|x|}. \tag{3}$$

The discrete spectrum consists of an infinite family of eigenvalues $E_k(h)$

$$E_k(h) = \frac{-1}{2h^2k^2},\ k \in \mathbb{N}, \tag{4}$$

each eigenvalue having multiplicity k^2. The spacing between successive eigenvalues is $\mathcal{O}(k^{-3})$.

With the choice of $h = 1/N$ and $k = N$, we see that $E_{k=N}(h = 1/N) = -1/2$ is in the spectra of the countable family of Hamiltonians $H_V(1/N)$, $N \in \mathbb{N}$. The multiplicity of the eigenvalue $-1/2$ grows as N^2.

The unscaled Stark hydrogen Hamiltonian is

$$\begin{aligned} H_V(h,F) &= -\frac{h^2}{2}\Delta - \frac{1}{|x|} + \epsilon(h) F x_1 \\ &= H_V(h) + w_h(F), \end{aligned} \tag{5}$$

where $F \geq 0$ is the electric field strength and we have chosen the x_1-direction for the field. We consider a parameter $\epsilon(h) = h^{K+\delta}$, for $0 < \delta < 1$. We will choose $K \in \mathbb{N}$ below.

The dilation group D_α, $\alpha > 0$, a representation of the multiplicative group $\mathbb{R}^+$, has a unitary implementation of $L^2(\mathbb{R}^d)$ given by

$$(D_\alpha f)(x) = \alpha^{d/2} f(\alpha x). \tag{6}$$

We scale the Hamiltonian in (5) by $\alpha = h^2$:

$$D_{h^2} H_V(h,F) D_{h^{-2}} = \frac{1}{h^2}\left(-\frac{1}{2}\Delta - \frac{1}{|x|} + h^4 \epsilon(h) F x_1 \right). \tag{7}$$

We call this rescaled Hamiltonian $S_h(F)$ so that

$$\begin{aligned} S_h(F) &= -\frac{1}{2}\Delta - \frac{1}{|x|} + h^4 \epsilon(h) F x_1 \\ &= H_V + h^4 \epsilon(h) F x_1, \end{aligned} \tag{8}$$

where we write $H_V \equiv H_V(1)$ and $W_h(F) = h^4 \epsilon(h) F x_1$ is the rescaled perturbation. Note that for $F = 0$, the eigenvalues of $S_h(0)$ are given by $E_k(1) = -1/(2k^2)$, with $k \in \mathbb{N}$. We will keep $F > 0$ fixed. The effective electric field is $h^4 \epsilon(h) F$ and we can make this small be taking $h \to 0$, or, equivalently, with $h = 1/N$, by taking $N \to \infty$.

3. Resonances of the Stark hydrogen Hamiltonian

The hydrogen atom Hamiltonian $H_V(h,F)$ with an external electric field Fx_1 is given in (5). We write $H_0(h,F)$ for the Stark Hamiltonian with $V = 0$. *For this section only, we take* $h = 1$ *and write* $H_V(F) = H_V(1,F)$*, for the hydrogen atom Stark Hamiltonian, and* $H_V = H_V(1,0)$*, when the field* $F = 0$*. The Stark Hamiltonian with* $V = 0$ *and* $h = 1$ *is denoted by* $H_0(F) = H_0(1,F) = -(1/2)\Delta + \epsilon(h) F x_1$*. and* $H_V = H_V(1,0)$. For $F \neq 0$, the spectrum of $H_V(F)$ is purely absolutely continuous and equal to $\mathbb{R}$. We are interested in the fate of the negative eigenvalues of H_V when the field F is turned on. We review the results of Herbst [4] on the resonances associated with the $F \neq 0$ case. Herbst's article deals with more general Stark Hamiltonians but we cite and use his results only for the hydrogen atom case of interest here for which V is the Coulomb potential.

3.1. **Dilation analyticity.**

The dilated Stark hydrogen Hamiltonian is obtained by conjugating (5) with the unitary dilation group D_α defined in (6). We take $\alpha = e^\theta > 0$, for $\theta \in \mathbb{R}$. We obtain

$$\begin{aligned} H_V(F,\theta) &= D_{exp(\theta)} H_V(F) D_{exp(-\theta)} \\ &= -\frac{e^{-2\theta}}{2}\Delta - \frac{e^{-\theta}}{|x|} + e^\theta F x_1. \end{aligned} \tag{9}$$

We are interested in extending this formula to θ with $\Im\theta \neq 0$. There are two properties that need to be checked: the analyticity of the potential, and the analyticity of the Stark Hamiltonian. Since the potential is a Coulomb potential, we have $V(\theta) = e^{-\theta}V$, so $V(\theta)$ is a type A analytic family of operators. Furthermore, as $V(-\Delta+1)^{-1}$ is a compact operator, it follows that $V(\theta)(-\Delta+1)^{-1}$ is a compact operator-valued analytic function of θ for $\theta \in \mathbb{C}$. In accordance with the Herbst's hypothesis [4, p. 287], we may take $\theta_0 = \pi/3$, the maximum width of the strip of analyticity allowed by the purely Stark Hamiltonian $H_0(F) = -(1/2)\Delta + Fx_1$. In order to understand the origin of the bound $\pi/3$, we note that for $F \in \mathbb{R}$

$$H_0(F,\theta) = -(1/2)e^{-2\theta}\Delta + Fe^{\theta}x_1 = e^{-2\theta}[-(1/2)\Delta + Fe^{3\theta}x_1]. \qquad (10)$$

Herbst proved results on the operator $-(1/2)\Delta + Fe^{3\theta}x_1$ when θ becomes complex in section II of [4]. The effective electric field $Fe^{3\theta}$ has a nonzero imaginary part, necessary for Herbst's results, only if $0 < |\Im\theta| < \pi/3$.

Herbst [4] proved the following theorem about the dilated operator $H_V(F,\theta)$. We consider $F > 0$ fixed.

We recall that for a closed operator with an isolated eigenvalue z_0, the algebraic multiplicity of the eigenvalue is defined as the dimension of the range of the corresponding Riesz projector.

Theorem 2. [4, Theorem III.2] *For $0 < \Im\theta < \pi/3$, the operator $H_V(F,\theta)$ is closed on $D(-\Delta) \cap D(M_{x_1})$. The operator family $H_V(F,\theta)$ is an analytic family of type A operators in θ. The spectrum on $H_V(F,\theta)$ is discrete, independent of θ, and the algebraic multiplicity of each eigenvalue is independent of θ.*

3.2. **Resonances.** Herbst [4] proved that for $V = 0$, the closed operator $H_0(F,\theta)$, $F \neq 0$, has no spectrum for $0 < |\Im\theta| < \pi/3$. As stated in Theorem 2, Herbst also showed, using the techniques of dilation analyticity, that for $0 < \Im\theta < \pi/3$, the non self-adjoint Hamiltonian $H_V(F,\theta)$, with V a Coulomb potential, has isolated eigenvalues with finite algebraic multiplicity. Furthermore, Herbst proved that these eigenvalues are connected to the eigenvalues of the $F = 0$ and $\Im\theta = 0$ operators.

Theorem 3. [4, Theorem III.3] *Suppose that E_0 is a negative eigenvalue of H_V, defined in (3) with $h = 1$, of multiplicity N_0. Then for $F > 0$ small, there are exactly N_0 eigenvalues, counting algebraic multiplicity, of $H_V(F,\theta)$, as defined in (9) with $0 < \Im\theta < \pi/3$, nearby, and as $F \to 0^+$, these converge to E_0.*

We also apply Theorems 2 and 3 to the scaled operator $S_h(F)$ defined in (8) with F of the theorem replaced by $h^4\epsilon(h)F$, and take $h = 1/N$. For any fixed $N \in \mathbb{N}$, we consider the resonance cluster $\{z_{N,j}(h,F)\}$ of $S_h(F,\theta)$ near the eigenvalue $-1/(2N^2)$ of $H_V(\theta)$. Note that the operator $S_h(F)$ has an effective electric field with strength $h^4\epsilon(h)F$ that vanishes as $h \to 0$. Hence, Theorem 3 states that the resonances $z_{N,j}(h,F)$ converge to the N^2-degenerate eigenvalue E_N as $h \to 0$.

3.3. **Resolvent estimates.** We summarize the resolvent estimates needed from [4]. We recall that for a closed operator A with domain $D(A)$, the *numerical range* of A, denoted $W(A)$, is the smallest convex set generated by $\{(u, Au) \mid u \in D(A)\}$. We let $H_0(F) = -(1/2)\Delta + Fx_1$ be the Stark Hamiltonian. Following Herbst [4], we review the results on Stark Hamiltonians with complex electric fields.

Proposition 1. [4, Theorem II.1] *We write $F = Ee^{i\phi}$, with $E, \phi \in \mathbb{R}$, $E \neq 0$, and $0 < |\phi| < \pi/3$.*

(1) *The spectrum of $H_0(F)$ is empty.*
(2) *The numerical range of $H_0(F)$ is the half-plane*

$$W(H_0(F)) = \left\{ z \in \mathbb{C} \mid \Re z > \left(\frac{\cos\phi}{\sin\phi} \right) \Im z \right\}, \tag{11}$$

independent of $E \neq 0$.
(3) *The resolvent is bounded*

$$\|(H_0(F) - z)^{-1}\| \leq [dist(z, W(H_0(F)))]^{-1}. \tag{12}$$

We now consider the dilated Stark Hamiltonian $H_0(1, F, \theta) \equiv H_0(F, \theta)$, as defined in (9),

$$H_0(F, \theta) = -(1/2)e^{-2\theta}\Delta + e^{\theta}Fx_1. \tag{13}$$

The following operator plays an important role in the analysis:

$$K(F, \theta, z) \equiv V(\theta)(H_0(F, \theta) - z)^{-1}, \tag{14}$$

where the dilated Coulomb potential is given by

$$V(\theta) = \frac{e^{-\theta}}{|x|}. \tag{15}$$

We prove a convergence estimate for $K(F, \theta, z) - K(0, \theta, z)$ with a precise rate of convergence as $F \to 0$ (recall that $h = 1$ here). This estimate is possible since the potential is a Coulomb potential.

We recall the basic resolvent estimates. Let $H_0(\theta) = -(1/2)e^{-2\theta}\Delta$, and $H_0(F, \theta) = -(1/2)e^{-2\theta}\Delta + Fe^{\theta}x_1$ be the Stark Hamiltonian. For any $F \neq 0$, we have the following basic estimate from Proposition 1:

$$\|(z - H_0(F, \theta))^{-1}\| \leq 1/d(z, W(H_0(F, \theta)). \tag{16}$$

Let γ_N be a simple closed contour about $\tilde{E}_N = -1/2N^2$ of radius $1/(8N^3)$. For $z \in \gamma_N$, we have

$$\|(z - H_0(\theta))^{-1}\| \leq 1/d(z, e^{-2\theta}\mathbb{R}^+) = \mathcal{O}(N^2). \tag{17}$$

The contour γ_N is chosen so that it contains only one eigenvalue $\tilde{E}_N$ of $H_V(\theta)$. Recall that $V(\theta)(H_0(\theta) + 1)^{-1}$ is a compact analytic operator valued function for $|\Im\theta| < \pi/3$.

Proposition 2. [4, Proposition III.1]

(1) *The operator $K(F, \theta, z)$ is compact and jointly analytic in (z, θ) on the region*

$$\{(\theta, z) \mid z \in \mathbb{C},\ 0 < |\Im\theta| < \pi/3\}. \tag{18}$$

(2) *We have the following convergence on the contour* γ_N *with* $0 < |\Im\theta| < \pi/3$*:*

$$\|K(F,\theta,z) - K(0,\theta,z)\| = \mathcal{O}(FN^4), \tag{19}$$

as $F \to 0$*. This convergence is uniform on the larger set* $\{(\theta,z) \mid d(z, W(H_0(F,\theta))) > 0,\ 0 < |\Im\theta| < \pi/3\}$.

We need the following lemma summarizing several key estimates on resolvents.

Lemma 1. *Let* $z \in \gamma_N$ *and* $0 < |\Im\theta| < \pi/3$.

(1) $\|(H_0(F,\theta) - z)^{-1}\| = \mathcal{O}(N^2)$
(2) $\|(H_0(\theta) - z)^{-1}\| = \mathcal{O}(N^2)$
(3) $\|V(\theta)(H_0(\theta) - z)^{-1}\| = \mathcal{O}(N)$
(4) $\|e^{-2\theta}p_1(H_0(\theta) - z)^{-1}\| = \mathcal{O}(N^2)$*, where* $p_1 = -i\partial/\partial x_1$.

Proof. 1. The first estimate follows from the bound (12) and the fact that the numerical range is a half-plane located a distance $\mathcal{O}(1/N^2)$ from the contour γ_N.
2. The second estimate follows similarly as the spectrum of $H_0(\theta)$ is the half line $e^{-2\Im\theta i}\mathbb{R}^+$, see (16).
3. The third estimate requires the following bound. Let C_3 denote the constant $C_3 = (2\pi)^{-3/2}(\int_{\mathbb{R}^3}(1+|p|^2)^{-2}\ d^3p)^{1/2}$. For any $\psi \in H^2(\mathbb{R}^3)$, and for any $\lambda > 0$, we have

$$\|\psi\|_\infty \le \frac{C_3}{\lambda^{1/2}}\|\Delta\psi\| + C_3\lambda^{3/2}\|\psi\|. \tag{20}$$

This follows from the Sobolev embedding theorem and standard estimates with the Fourier transform. We decompose the Coulomb potential as $V = V\chi_{B_N(0)} + V(1-\chi_{B_N(0)}) \equiv V_2 + V_\infty$, where $\chi_{B_N(0)}$ is the characteristic function on the ball of radius $N > 0$ centered at the origin. We have that $V_2 \in L^2(\mathbb{R}^3)$ and $V_\infty \in L^\infty(\mathbb{R}^3)$, with $\|V_2\| = \omega_3^{1/2}N^{1/2}$ and $\|V_\infty\|_\infty = 1/N$. With the help of (20), and choosing $\lambda = 1/N$, we write

$$\begin{aligned}\|V\psi\| &\le \|V_2\|\|\psi\|_\infty + \|V_\infty\|_\infty\|\psi\| \\ &\le (\omega_3 N)^{1/2}C_3\|\Delta\psi\| + (\omega_3^{1/2}C_3 + 1)N^{-1}\|\psi\|, \end{aligned} \tag{21}$$

where $\omega_3 = 4\pi$. Recall that $(H_0(\theta) - z)^{-1} : L^2(\mathbb{R}^3) \to H^2(\mathbb{R}^3)$ and that $|z| = \mathcal{O}(N^{-2})$ for $z \in \gamma_N$. Taking estimate (21) with $\psi = (H_0(\theta) - z)^{-1}\phi$, for any $\phi \in L^2(\mathbb{R}^3)$, together with estimate (2), we easily obtain estimate (3).
4. The proof of estimate (4) follows from

$$\|e^{-2\theta}p_1(H_0(\theta) - z)^{-1}\| \le \max\left\{|p_1(|p|^2 - e^{2\theta}z)^{-1}\right\} = \mathcal{O}(N^2), \tag{22}$$

since $z \in \gamma_N$.

□

We can now give the proof of Proposition 2.

Proof. 1. As in Herbst [4], we write

$$K(F,\theta,z) = V(\theta)(-\Delta + 1)^{-1}J(\theta,z), \tag{23}$$

where

$$J(\theta, z) = (-\Delta + 1)(H_0(F, \theta) - z)^{-1}. \tag{24}$$

The Coulomb potential has the property that $V(\theta)(-\Delta + 1)^{-1}$ is an analytic, compact operator-valued function for any $\theta \in \mathbb{C}$. The quadratic estimate (147) implies that $J(\theta, z)$ is bounded. For an appropriately defined circle γ, a contour integral representation

$$J(\theta, z) = (2\pi i)^{-2} \int_\gamma \int_\gamma dw \; d\phi (w - z)^{-1} (\phi - \theta)^{-1} J(\phi, w) \tag{25}$$

is used to verify that $J(\theta, z)$ is analytic in the region described in the proposition: $0 < |\Im\theta| < \pi/3$ and $z \in \mathbb{C}$.

2. Using the resolvent formula, we write the difference on the left in (19) as

$$\begin{aligned} & K(F, \theta, z) - K(0, \theta, z) \\ = \; & -Fe^\theta x_1 V(\theta)(H_0(\theta) - z)^{-1}(H_0(F, \theta) - z)^{-1} \\ & +Fe^\theta V(\theta)(H_0(\theta) - z)^{-1}[H_0(\theta), x_1](H_0(\theta) - z)^{-1}(H_0(F, \theta) - z)^{-1}. \end{aligned} \tag{26}$$

The commutator $[H_0(\theta), x_1] = -2e^{-2\theta} ip_1$, where $p_1 = -i\partial/\partial x_1$. Note that $\|x_1 V(\theta)\| \leq e^{-\Re\theta}$, since the potential is Coulombic. From the resolvent estimates in Lemma 1, we obtain

$$\|K(F, \theta, z) - K(\theta, z)\| \leq Fe^{\Re\theta} \|(H_0(F, \theta) - z)^{-1}\| \{A + B\}, \tag{27}$$

where

$$A = e^{-\Re\theta} \|(H_0(\theta) - z)^{-1}\| = \mathcal{O}(N^2), \tag{28}$$

and

$$B = \|V(\theta)(H_0(\theta) - z)^{-1}\| + 2\|e^{-2\theta} p_1 (H_0(\theta) - z)^{-1}\| = \mathcal{O}(N^2). \tag{29}$$

Consequently, we find from (27)–(29) that

$$\|K(F, \theta, z) - K(0, \theta, z)\| = \mathcal{O}(FN^4). \tag{30}$$

This proves part (2) of the proposition. □

We recall that our F is $Fh^4\epsilon(h)$ so that with $h = 1/N$ and $\epsilon(h) = h^{K+\delta}$, part (2) of Proposition 2 states that uniformly for $z \in \gamma_N$, with $|\gamma_N| = 2\pi(8N^3)^{-1}$, we have

$$\|K(F, \theta, z) - K(0, \theta, z)\| = \mathcal{O}(N^{-K-\delta}), \tag{31}$$

as $N \to \infty$.

4. A semiclassical trace identity for resonance clusters

We now return to the scaled Hamiltonian $S_h(F) = H_V + W_h(F)$, with $F > 0$ fixed, the perturbation $W_h(F) = h^4\epsilon(h)F$, with $\epsilon(h) = h^{K+\delta}$, and $K \geq 6$. We will take $h = 1/N$ and consider $N \to \infty$. We need a basic trace identity relating the resonance shifts $z_{N,j}(1/N, F) - E_N(1/N)$, with $E_N(1/N) = -1/2$, to the eigenvalues of a reduced, finite dimensional matrix obtained from the Stark perturbation $W_h(F)$. This is the main result of this section stated in Theorem 4.

In section 3, the dilation was written as e^{θ}. The real part of θ does not affect Theorems 2 and 3. Consequently, *we will now write the dilation as* $e^{i\theta}$, *with* $\theta \in \mathbb{R}$ *and in the range* $0 < |\theta| < \pi/3$. The operators are obtained by analytic continuation as discussed in section 3.

As above, we fix $N \in \mathbb{N}$. We study the non self-adjoint operator $S_h(F, \theta)$ obtained from $S_h(F)$ in (8) by dilation $D_{exp(i\theta)}$, for $\theta \in \mathbb{R}$ as above:

$$S_h(F, \theta) = D_{exp(i\theta)} S_h(F) D_{exp(-i\theta)} = H_V(\theta) + W_h(F, \theta), \tag{32}$$

where the dilated, scaled hydrogen atom Hamiltonian is

$$H_V(\theta) = D_{exp(i\theta)} H_V D_{exp(-i\theta)} = -\frac{e^{-2i\theta}}{2}\Delta - \frac{e^{-i\theta}}{|x|}, \tag{33}$$

and the dilated perturbation is

$$W_h(F, \theta) = D_{exp(i\theta)} W_h(F) D_{exp(-i\theta)} = h^4 \epsilon(h) e^{i\theta} F x_1. \tag{34}$$

We write $W_h(F) = W_h(F, 0)$ and note that $W_h(F) = h^4\epsilon(h) F x_1$ is self-adjoint.

Let Π_N^0 be the orthogonal projector for the eigenvalue $\tilde{E}_N = -1/(2N^2)$ of the scaled hydrogen atom Hamiltonian H_V defined in (8). Under dilation, these remain eigenvalues of $H_V(\theta)$. Let $P_N(\theta)$ be the projector for the resonance cluster $\{\tilde{z}_{N,i}(h, F)\}$ near $\tilde{E}_N$ of the non self-adjoint operator $S_h(F, \theta)$. We write for the resonance shift

$$\tilde{z}_{N,i}(1/N, F) = \tilde{E}_N + \nu_{N,i}, \ \ \nu_{N,i} \in \mathbb{C}. \tag{35}$$

The following trace estimate for the resonance shifts is the main result of this section.

Theorem 4. *Let* $\nu_{N,i}$ *be the complex resonance shifts defined in (35), and let* $\tau_{N,i}$ *be the eigenvalues of the self-adjoint operator* $\Pi_N^0 W_h(F) \Pi_N^0$. *For any* $m \in \mathbb{N}$, *and for* $h = 1/N$, *we have the following trace formula:*

$$\frac{1}{d_N}\sum_{i}^{d_N}\left(\frac{\nu_{N,i}}{h^2\epsilon(h)}\right)^m = \frac{1}{d_N}\sum_{i=1}^{d_N}\left(\frac{\tau_{N,i}}{h^2\epsilon(h)}\right)^m + \mathcal{O}\left(\frac{1}{N^{\beta}}\right), \tag{36}$$

for some $\beta > 0$.

The proof of Theorem 4 requires two main steps. In the first, we express the left side of (36) in terms of the trace of the operator $P_N(\theta)(S_h(F, \theta) - \tilde{E}_N)^m P_N(\theta)$. In the second step, we evaluate the trace of this operator and express it in terms of the finite-rank operator $\Pi_N^0 W_h(F) \Pi_N^0$.

4.1. **Step 1. A trace calculation.** Since $S_h(F, \theta)$ is non self-adjoint, the projector $P_N(\theta)$ is not self-adjoint. The range of $P_N(\theta)$ is a finite-dimensional subspace $\mathcal{E}_N$ with a dimension N^2 that is equal to the geometric multiplicity of the eigenvalue $\tilde{E}_N$ of H_V. Let $\tilde{z}_{N,j}(h, F)$, $j = 1, \ldots, K$, with $1 \leq K \leq N^2$ be a listing of the **distinct** resonances that converge to $\tilde{E}_N$ as $N \to \infty$. Let $P_{N,j}(\theta)$ be the projector onto the generalized eigenspace $\mathcal{E}_{N,j}$ corresponding to the resonance $\tilde{z}_{N,j}(h, F)$. The subspace $\mathcal{E}_N$ admits a direct sum decomposition $\mathcal{E}_N = \oplus_{j=1}^K \mathcal{E}_{N,j}$, where the finite-dimensional subspaces $\mathcal{E}_{N,j}$, $j = 1, \ldots, K$ have the following properties:

(1) $\mathcal{E}_{N,j} = \text{ran } P_{N,j}(\theta)$ and $\dim \mathcal{E}_{N,j} = m_j$
(2) $P_N(\theta) = \sum_{j=1}^K P_{N,j}(\theta)$
(3) the algebraic multiplicity of the resonance $z_{N,j}$ is given by m_j
(4) $N^2 = \sum_{j=1}^K m_j$
(5) the projectors satisfy $P_{N,j}(\theta) P_{N,m}(\theta) = \delta_{jm} P_{N,j}(\theta)$
(6) on the invariant subspace $\mathcal{E}_{N,j}$, we have $S_h(F,\theta)|\mathcal{E}_{N,j} = \tilde{z}_{N,j} I_{\mathcal{E}_{N,j}} + D_{N,j}$, where $D_{N,j}$ is nilpotent with order m_j and commutes with $S_h(F,\theta)$
(7) $\ker(S_h(F,\theta) - \tilde{z}_{N,j})^{m_j} = \mathcal{E}_{N,j}$.

We refer to Kato [5, chapter III, section 6.5] for proofs of all these properties.

The main part of the proof of step 1 is the evaluation of the trace

$$Tr\left(P_N(\theta)(S_h(F,\theta) - \tilde{E}_N)^m P_N(\theta)\right). \tag{37}$$

Using the facts listed above, we find

$$\begin{aligned} Tr\left(P_N(\theta)(S_h(F,\theta) - \tilde{E}_N)^m P_N(\theta)\right) &= \sum_{j=1}^K Tr\left(P_{N,j}(\theta)(S_h(F,\theta) - \tilde{E}_N)^m P_{N,j}(\theta)\right) \\ &= \sum_{j=1}^K Tr\left(P_{N,j}(\theta)(\tilde{z}_{N,j}(h,F) - \tilde{E}_N + D_{N,j})^m P_{N,j}(\theta)\right) \\ &= \sum_{j=1}^K (\tilde{z}_{N,j}(h,F) - \tilde{E}_N)^m Tr P_{N,j} \\ &= \sum_{j=1}^K m_j (\tilde{z}_{N,j}(h,F) - \tilde{E}_N)^m \\ &= \sum_{j=1}^K m_j (\nu_{N,j})^m. \end{aligned} \tag{38}$$

We also used the facts that $Tr P_{N,j}(\theta) = m_j$, and that $Tr P_{N,j}(\theta) D_{N,j} = 0$, since $D_{N,j}$ is nilpotent and $D_{N,j} P_{N,j} = P_{N,j} D_{N,j} = D_{N,j}$.

The distinct complex resonance shifts $\nu_{N,j}$ are defined in (35). We now change notation and list the shifts with multiplicity included. That is, $\nu_{N,j}$ is listed m_j times. It then follows directly from (38) that

$$Tr\left(\frac{P_N(\theta)(S_h(F,\theta) - \tilde{E}_N)^m P_N(\theta)}{(h^2\epsilon(h))^m}\right) = \sum_{i=1}^{d_N} \left(\frac{\nu_{N,i}}{h^2\epsilon(h)}\right)^m. \tag{39}$$

4.2. **Step 2. Evaluation of the trace.** The second step in the proof of Theorem 4 is to estimate the trace on the left side of (39). This requires that we replace $P_N(\theta)$ by $\Pi_N^0(\theta)$ and that we control the perturbation $W_h(F,\theta)$ defined in (34).

In order to replace the projector $P_N(\theta)$ by $\Pi_N^0(\theta)$, we need some results relating the projector $\Pi_N^0(\theta)$ to $P_N(\theta)$ as $N \to \infty$, which means that $h = 1/N \to 0$.

Lemma 2. *For fixed $\theta \in \mathbb{R}$ with $0 < \theta < \pi/3$, we have*

$$\|\Pi_N^0(\theta) - P_N(\theta)\| = \mathcal{O}(N^{6-K-\delta}), \tag{40}$$

for $K \geq 3$ and $\delta > 0$. Consequently, if $P^\perp \equiv 1 - P$, we have

(1) $\|(\Pi_N^0)^\perp(\theta) P_N(\theta)\| = \mathcal{O}(N^{6-K-\delta})$,
(2) $\|P_N^\perp(\theta)\Pi_N^0(\theta)\| = \mathcal{O}(N^{6-K-\delta})$.

Proof. 1. We consider the contour γ_N, a circle of radius $1/(8N^3) > 0$ about the eigenvalue $\tilde{E}_N$. We write the projectors as contour integrals

$$\Pi_N^0(\theta) - P_N(\theta) = \frac{1}{2\pi i}\int_{\gamma_N} dz[(z - H_V(\theta))^{-1} - (z - S_h(F,\theta))^{-1}]. \tag{41}$$

Recall that $S_h(F,\theta) = H_V(\theta) + W_h(F,\theta)$, and that $H_0(h,F,\theta) = -(1/2)e^{-2i\theta}\Delta + W_h(F,\theta)$. We define a kernel (as in section 3)

$$K_h(F,\theta,z) = V(\theta)(H_0(h,F,\theta) - z)^{-1}. \tag{42}$$

From the second resolvent identity for $H_0(h,F,\theta)$ and $S_h(F,\theta)$, we obtain

$$(z - S_h(F,\theta))^{-1} = (z - H_0(h,F,\theta))^{-1}(1 + K_h(F,\theta,z))^{-1}, \tag{43}$$

whenever the inverse on the right exists. Substituting this back into the second resolvent identity for $H_0(h,F,\theta)$ and $S_h(F,\theta)$, we obtain

$$\frac{1}{z - S_h(F,\theta)} - \frac{1}{z - H_0(h,F,\theta)} = -\frac{1}{z - H_0(h,F,\theta)}\frac{1}{1 + K_h(F,\theta,z)}K_h(F,\theta,z). \tag{44}$$

We note a similar identity for $h = 0$ comparing $H_V(\theta) = H_0(\theta) + V(\theta)$ with $H_0(\theta) = -(1/2)e^{-2i\theta}\Delta$. We let $K_0(\theta,z) \equiv V(\theta)(H_0(\theta) - z)^{-1}$ in analogy with (42) for $F = 0$.

$$\frac{1}{z - H_V(\theta)} - \frac{1}{z - H_0(\theta)} = -\frac{1}{z - H_0(\theta)}\frac{1}{1 + K_0(\theta,z)}K_0(\theta,z). \tag{45}$$

2. We subtract (44) from (45) and substitute the difference into the integral in (41). Since both $(z - H_0(h,F,\theta))^{-1}$ and $(z - H_0(\theta))^{-1}$ are analytic on and inside γ_N, their contribution to the contour integral vanishes. Consequently, the difference of the projections in (41) is equal to the contour integral

$$\frac{1}{2\pi i}\int_{\gamma_N} dz \left[\frac{1}{z - H_0(h,F,\theta)}K_h(F,\theta,z)\frac{1}{1 + K_h(F,\theta,z)} - \frac{1}{z - H_0(\theta)}K_0(\theta,z)\frac{1}{1 + K_0(\theta,z)}\right]. \tag{46}$$

From Proposition 2, part (2), we have that $K_h(F,\theta,z)$ and $K_0(\theta,z)$ are compact and that $K_h(F,\theta,z) \to K_0(\theta,z)$ in norm. We also use the fact that $(z - H_0(h,F,\theta))^{-1} \to (z - H_0(\theta))^{-1}$ strongly as $h \to 0$. We rewrite the integrand in

(46) as a sum of three terms:

$$I \equiv \frac{1}{z - H_0(h,F,\theta)}[K_h(F,\theta,z) - K_0(\theta,z)]\frac{1}{1+K_h(F,\theta,z)} \tag{47}$$

$$II \equiv \left[\frac{1}{z - H_0(h,F,\theta)} - \frac{1}{z - H_0(\theta)}\right] K_0(\theta,z)\frac{1}{1+K_0(\theta,z)} \tag{48}$$

$$III \equiv \frac{1}{z - H_0(h,F,\theta)}K_0(\theta,z)\left[\frac{1}{1+K_h(F,\theta,z)} - \frac{1}{1+K_0(\theta,z)}\right]. \tag{49}$$

3. We need estimates on the operators $K_0(\theta, z)$ and $K_h(F, \theta, z)$ and their resolvents at -1 that appear in (47), (48), and (49). We begin with the estimates for $K_0(\theta, z)$. From part (3) of Lemma 1, we have

$$\|K_0(\theta,z)\| = \mathcal{O}(N). \tag{50}$$

From the definition of $K_0(\theta, z)$, we easily find that

$$(1 + K_0(\theta,z))^{-1} = 1 - V(\theta)(H_0(\theta) + V(\theta) - z)^{-1}. \tag{51}$$

Recall that the Coulomb potential V is relatively H_0-bounded with relative bound less than one. So there exist constants $0 < a < 1$ and $b > 0$, so that for all $u \in H^2(\mathbb{R}^3)$, we have

$$\|Vu\| \leq a\|H_0 u\| + b\|u\|. \tag{52}$$

Scaling by $e^{i\theta}$, with $\theta \in \mathbb{R}$, we find

$$\|V(\theta)u\| \leq a\|H_0(\theta)u\| + b\|u\|. \tag{53}$$

Replacing u by $R_V(\theta)w = (H_0(\theta) + V(\theta) - z)^{-1}w$, for $z \in \gamma_N$ and $w \in L^2(\mathbb{R}^3)$, we obtain

$$\|V(\theta)R_V(\theta)w\| \leq a\|w\| + (a|z| + b)\|R_V(\theta)w\| + a\|V(\theta)R_V(\theta)w\|. \tag{54}$$

Since $0 < a < 1$ and $|z| = \mathcal{O}(N^{-2})$, we obtain

$$\|V(\theta)R_V(\theta)\| \leq C_1 + C_2\|R_V(\theta)\|. \tag{55}$$

It follows from (51), (55), and the fact that $\|R_V(\theta)\| = \mathcal{O}(N^3)$ that

$$\|(1 + K_0(\theta,z))^{-1}\| = \mathcal{O}(N^3). \tag{56}$$

4. The second estimate we need concerns $1 + K_h(F, \theta, z)$. We write

$$\begin{aligned} 1 + K_h(F,\theta,z) &= [1 + K_0(\theta,z)] \\ &\quad \times[1 + (1 + K_0(\theta,z))^{-1}(K_h(F,\theta,z) - K_0(\theta,z))], \end{aligned} \tag{57}$$

from which it follows that

$$(1 + K_h(F,\theta,z))^{-1} = [1 + M_h(F,\theta,z)]^{-1}[1 + K_0(\theta,z)]^{-1}, \tag{58}$$

where

$$M_h(F,\theta,z) = (1 + K_0(\theta,z))^{-1}(K_h(F,\theta,z) - K_0(\theta,z)). \tag{59}$$

It follows from part (2) of Proposition 2 and (56) that

$$\|M_h(F,\theta,z)\| = \mathcal{O}(N^{3-K-\delta}), \tag{60}$$

so if $K \geq 3$, this term is less than $1/2$ for all N large. It follows from (58) that

$$\|(1 + K_h(F,\theta,z))^{-1}\| = \mathcal{O}(N^3). \tag{61}$$

5. We estimate each term I, I, and III in (47), (48), and (49), uniformly in $z \in \gamma_N$, using the estimate of Proposition 2. For the first term I in (47), we use part (1) of Lemma 1, part (2) of Proposition 2, and (61), to obtain for $K \geq 3$:

$$\|I\| = \mathcal{O}(N^2 \cdot N^{-K-\delta} \cdot N^3) = \mathcal{O}(N^{5-K-\delta}). \tag{62}$$

As for II in (48), we use the quadratic estimate in [4, Proposition II.4] (presented in appendix 8) in order to prove the bound

$$\|x_1(H_0(h,F,\theta) - z)^{-1}\| = \mathcal{O}(1), \ z \in \gamma_N. \tag{63}$$

Recalling that $H_0(h,F,\theta) - H_0(\theta) = W_h(F,\theta) = h^4 \epsilon(h) e^{i\theta} F x_1$, we find that

$$\|II\| = \mathcal{O}(N^{-4-K-\delta} \cdot N^2 \cdot N \cdot N^3) = \mathcal{O}(N^{2-K-\delta}). \tag{64}$$

Recalling that $K \geq 3$, we see that the term II vanishes uniformly on γ_N as $N \to \infty$.

Finally, for the last term III in (49), part (1) of Lemma 1, estimate (50), together with (61), (56) and part (2) of Proposition 2, yield

$$\begin{aligned} \|III\| &= \mathcal{O}(N^2 \cdot N \cdot N^3 \cdot N^{-K-\delta} \cdot N^3) \\ &= \mathcal{O}(N^{9-K-\delta}). \end{aligned} \tag{65}$$

6. The difference of the projectors on the left side of (40) may be estimated from (46) and the above estimates, recalling that $|\gamma_N| = 2\pi(1/(8N^3))$:

$$\|\Pi_N^0(\theta) - P_N(\theta)\| \leq |\gamma_N|(\|I\| + \|II\| + \|III\|) = \mathcal{O}(N^{6-K-\delta}), \ K \geq 3. \tag{66}$$

So for $K \geq 6$, we obtain the vanishing of the difference as $N \to \infty$. Parts (1) and (2) of the lemma follow from (40) simply by writing

$$(\Pi_N^0(\theta))^\perp P_N(\theta) = (\Pi_N^0(\theta))^\perp (P_N(\theta) - \Pi_N^0(\theta)), \tag{67}$$

and similarly for part (2). □

4.3. **Step 3. Estimates on dilated coherent states.** In order to control the perturbation $W_h(F,\theta)$, we need estimates on the following operators: $\Pi_N^0(\theta) W_h(F,\theta) \Pi_N^0(\theta)$, $\Pi_N^0(\theta) W_h(F,\theta)$, and the operators $P_N(\theta)(S_h(F,\theta) - \tilde{E}_N) P_N(\theta)$ and $P_N(\theta)(S_h(F,\theta) - \tilde{E}_N)\Pi_N^0(\theta)$. Estimates on the first two operators are given in Lemma 3, and on the second two operators are given in Lemma 4.

Heuristically, we are able to control the first two operators due to the fact that the matrix elements of moments of the position operator $\|x\|$ in the eigenstates $\psi_N(\theta)$ of $H_V(\theta)$ satisfy

$$\langle \psi_N(\theta), \|x\|^m \psi_N(\theta) \rangle \sim N^{2m}. \tag{68}$$

This decay is due to the fact that the eigenstate is well localized about the Bohr radius and the Bohr radius scales like N^2. A proof of this localization property of the eigenfunctions is given in the Appendix 2 in section 7. This localization, however, is too weak to control the operator norm of the operators $\Pi_N^0(\theta) W_h(F,\theta) \Pi_N^0(\theta)$ and $\Pi_N^0(\theta) W_h(F,\theta)$. Using (68), we easily arrive at estimates of the type

$$\|\Pi_N^0(\theta) W_h(F,\theta) \Pi_N^0(\theta)\| = \mathcal{O}(N^2 \epsilon(h) h^2), \tag{69}$$

and the N^2 growth will not allow control of the trace in (36) since this is divided by $h^2 \epsilon(h)$. Instead of using (68), we use coherent states $\Psi_{\alpha,N}$ that form an overdetermined basis set of functions for the eigenspace of the hydrogen atom Hamiltonian corresponding to the eigenvalue $\tilde{E}_N$. These coherent states were described in detail in the papers of Bander and Itzykson [1] and more recently in [7, 8]. We recall the main points that we need here in Appendix 1, section 6. Recall that the dimension of the range of the projector $\Pi_N^0(\theta)$ is N^2 and that $\epsilon(h) = h^{K+\delta}$, for $K \geq 6$.

We use the following notation for operators that occur as remainder terms and that have bounds depending on h but uniform with respect to any other parameters. Let $K(g(h))$, for a function $g(h)$, denote a bounded operator with

$$\|K(g(h))\| = \mathcal{O}(g(h)). \tag{70}$$

an example of a function $g(h)$ is $(\epsilon(h)h^2)^m$. We will also write $K(\mathcal{O}(h^{-\ell}))$ to mean a bounded linear operator with $\|K(\mathcal{O}(h^{-\ell}))\| = \mathcal{O}(h^{-\ell})$. The actual form of K is unimportant and may vary from line to line but a bound of the type (70) or of the type $\mathcal{O}(h^{-\ell})$ will always hold.

Lemma 3. *There exists a constant $r_0 > 1$, independent of θ with $|\theta| < \pi/4$, so that for any $n \in \mathbb{N}$, we have*

$$\begin{aligned} \Pi_N^0(\theta) D_{N^2}^{-1} \|x\|^n D_{N^2} \Pi_N^0(\theta) &= \Pi_N^0(\theta) D_{N^2}^{-1} \|x\|^n \chi_{\|x\| \leq r_0} D_{N^2} \Pi_N^0(\theta) \\ &\quad + \Pi_N^0 K(\mathcal{O}(N^{-\infty})), \end{aligned} \tag{71}$$

where $\chi_{\|x\| \leq r_0}$ is the characteristic function on the set $\{x \in \mathbb{R}^3 \mid \|x\| \leq r_0\}$. As a consequence, we have the following estimates on the perturbation restricted to the eigenspace of $H_V(\theta)$:

(1) $\|\Pi_N^0(\theta) W_h(F,\theta) \Pi_N^0(\theta)\| = \mathcal{O}(N^{-K-2-\delta}) = \mathcal{O}(\epsilon(h)h^2)$,
(2) $\|\Pi_N^0(\theta) W_h(F,\theta)\| = \mathcal{O}(N^{-K-2-\delta}) = \mathcal{O}(\epsilon(h)h^2)$.

Proof. As mentioned above, the key to controlling the perturbation is the strong localization property of the coherent states. Coherent states for the hydrogen atom are reviewed in section 6. We prove below that the dilated coherent states $\Psi_{\alpha,N}(e^{i\theta}x)$ are L^2-valued analytic functions of θ provided $|\Re\theta| < \pi/4$ and provide uniform bounds. Since, as above, $\Im\theta$ pays no role in the calculations, we set $\Im\theta = 0$.

1. We first prove a decay estimate for the dilated coherent states that is the analog of [7, Lemma 4.1]. We prove that there exists a constant $r_0 > 1$, independent of $\alpha \in \mathcal{A}$, $N \in \mathbb{N}$, and $|\theta| < \pi/4$, so that for all $n, s \in \mathbb{N}$,

$$\lim_{N \to \infty} N^s \int_{\|x\| > r_0} \|x\|^n |D_{N^2} \Psi_{\alpha,N}(e^{i\theta}x)|^2 \, d^3x = 0. \tag{72}$$

This estimate implies that

$$\left| \int_{\mathbb{R}^3} \Psi_{\beta,N}^*(e^{i\theta}x) D_{N^2}^{-1} \|x\|^n \chi_{\|x\| > r_0} D_{N^2} \Psi_{\alpha,N}(e^{i\theta}x) \, d^3x \right| = \mathcal{O}(N^{-\infty}). \tag{73}$$

This estimate is uniform with respect to $\alpha, \beta \in \mathcal{A}$. We turn to the proof of (72). For any $b \in \mathbb{S}^2$, we will prove

$$\lim_{N \to \infty} N^s \int_{|x \cdot b| \geq r_0/2} |x \cdot b|^n |D_{N^2} \Psi_{\alpha,N}(e^{i\theta}x)|^2 \, d^3x = 0. \tag{74}$$

By making appropriate choices of b we recover (72) by a finite sum. Following the proof of [7, Lemma 4.1], we first prove that for any $q \geq 0$, there exist constants $c_2, c_3 > 0$, independent of θ, α and N, so that

$$\left(\int_{\mathbb{R}^3} |x \cdot b|^{2q} |D_{N^2} \Psi_{\alpha,N}(e^{i\theta} x)|^2 \; d^3x \right)^{1/2} \leq \frac{c_3 q! N^{1/2} e^{c_2 N}}{(N/240)^q}, \tag{75}$$

for any $b \in \mathbb{S}^2$. We repeat the argument from [7, Lemma 4.1] showing how the estimate (75) implies (74). Given n and s from (74), we take $m \in \mathbb{N}$ so that $N - 1 < m + n < N$ and set $q = (n+m)/2$. Since $|x \cdot b| \geq r_0/2$, we use Chebyshev's inequality and Stirling's formula for $q!$ to estimate (74) from (75),

$$\begin{aligned} & N^s \int_{|x \cdot b| \geq r_0/2} |x \cdot b|^n |D_{N^2} \Psi_{\alpha,N}(e^{i\theta} x)|^2 \; d^3x \\ \leq \; & \frac{N^s}{(r_0/2)^m} \int_{\mathbb{R}^3} |x \cdot b|^{m+n} |D_{N^2} \Psi_{\alpha,N}(e^{i\theta} x)|^2 \; d^3x \\ \leq \; & \frac{N^s}{(r_0/2)^m} \left[c_3 q! N^{1/2} (N/240)^{-q} e^{N c_2} \right]^2 \\ \leq \; & \frac{c_5 N^{s+3}}{(r_0/2)^{N-1-n}} e^{N c_4}, \end{aligned} \tag{76}$$

where $c_4 \equiv 2c_2 + \log 120 - 1 > 0$. We choose $r_0 > 2$ so that $r_0/2 > e^{2c_4}$ so that the right side of (76) is bounded by

$$c_6 N^{s+3} e^{-N c_4}, \tag{77}$$

and this vanishes as $N \to \infty$. This proves (74).

2. To prove (75), we change to the momentum variable (see (135)) so that

$$\begin{aligned} & \|(x \cdot b)^q D_{N^2} \Psi_{\alpha,N}(e^{i\theta} \cdot)\|^2 \\ = \; & \int_{\mathbb{R}^3} \left| \left(\frac{1}{N} b \cdot \nabla_p \right)^q \left(\frac{2}{e^{-2i\theta} \|p\|^2 + 1} \right)^2 a(N-1) (\alpha \cdot \omega(e^{-i\theta} p))^{N-1} \right|^2 \; d^3p. \end{aligned} \tag{78}$$

We next use the fact that $b \cdot \nabla_p$ generates translations in p so that for $z \in \mathbb{C}$,

$$\begin{aligned} & e^{(z/N) b \cdot \nabla_p} \left(\frac{2}{e^{-2i\theta} \|p\|^2 + 1} \right)^2 a(N-1) (\alpha \cdot \omega(e^{-i\theta} p))^{N-1} \\ = \; & \left(\frac{2}{e^{-2i\theta} \left(p + (z/N) b\right)^2 + 1} \right)^2 a(N-1) (\alpha \cdot \omega(e^{-i\theta} (p + (z/N) b))^{N-1} \end{aligned} \tag{79}$$

We need some estimates. First, in order to guarantee that the function in (79) remains in $L^2(\mathbb{R}^3)$, we observe that if $|z|/N < 1/120$ and $|\theta| < \pi/4$, there are finite constants $0 < C_1, C_2$ so that

$$\left| \frac{2 e^{2i\theta}}{(p + (z/N) b)^2 + e^{2i\theta}} \right|^2 \leq \begin{cases} \left(\frac{C_1}{\|p\|^2 + 1} \right)^2 & \|p\| > 2 \\ C_2 & \|p\| \leq 2. \end{cases} \tag{80}$$

This estimate is proved by estimating the absolute values of the real and imaginary parts of $(p + (z/N) b)^2 + e^{2i\theta}$ from below. So provided all other factors are uniformly bounded in p, the function in (79) is square integrable. Next, we prove the uniform bounds on the other factors for $|z|/N < 1/2$ and $|\theta| < \pi/3$. These conditions are less restrictive than needed for (80). We note that

$$|\alpha \cdot \omega(e^{-i\theta} p)| \leq \sqrt{10}, \tag{81}$$

for $|\theta| < \pi/3$ since $|\alpha| = \sqrt{2}$. In order to estimate ω, we expand about p and write

$$\omega(e^{-i\theta}(p + (z/N)b)) = \omega(e^{-i\theta} p) + \nabla_p \omega(e^{-i\theta}\tilde{p}) \cdot (z/N) e^{-i\theta} b, \tag{82}$$

for some $\tilde{p}$. It is easy to check that for $|z|/N < 1/2$, the gradient term satisfies

$$|\nabla_p \alpha \cdot \omega(e^{-i\theta}(p + (z/N)b))| \leq c_1, \tag{83}$$

so that

$$|\alpha \cdot \omega(e^{-i\theta}(p + (z/N)b))| \leq \sqrt{10}(1 + c_2|z|/N). \tag{84}$$

Consequently, for any N and $z \in \mathbb{C}$ so that $|z|/N < 1/2$, we have

$$|\alpha \cdot \omega(e^{-i\theta}(p + (z/N)b))|^{N-1} \leq c_0^N e^{c_2|z|}, \tag{85}$$

for absolute constants $c_0, c_1 > 0$. Combining these, we obtain

$$\left\| e^{(z/N)b\cdot\nabla_p} \left(\frac{2}{e^{-2i\theta}\|p\|^2 + 1} \right)^2 a(N-1)(\alpha \cdot \omega(e^{-i\theta} p))^{N-1} \right\| \leq c_3 N^{1/2} c_0^N e^{c_2|z|}, \tag{86}$$

since $a(N-1) \sim \sqrt{N-1}$.

3. We now use Cauchy's theorem, with estimate (86), in order to estimate (78), by integrating over a path in the z-plane of radius $N/240 < N/120$ about the origin so that estimate (80) is valid. This gives

$$\begin{aligned} &\|(x \cdot b)^q D_{N^2} \Psi_{\alpha,N}(e^{i\theta} \cdot)\| \\ &\leq \frac{q!}{2\pi} \int_{|z|=N/240} \frac{|dz|}{|z|^{q+1}} \left\| e^{(z/N)b\cdot\nabla_p} \left(\frac{2}{e^{-2i\theta}\|p\|^2 + 1} \right)^2 a(N-1)(\alpha \cdot \omega(e^{-i\theta} p))^{N-1} \right\| \\ &\leq \frac{c_3 q! N^{1/2} e^{c_2 N}}{(N/240)^q}, \end{aligned} \tag{87}$$

where the finite constant $c_2 > 0$ is a function of c_0 and c_1. This establishes (75).

4. It follows from estimate (72) that for $\alpha, \beta \in \mathcal{A}$, we have

$$\langle \Psi_{\alpha,N}, D_{N^2}^{-1} \|x\|^n \chi_{\|x\| > r_0} D_{N^2} \Psi_{\beta,N} \rangle = \mathcal{O}(N^{-\infty}), \tag{88}$$

where the error is uniform over $\mathcal{A} \times \mathcal{A}$. Of importance for us is that this estimate (88) implies that the moments of the position operator in coherent states satisfy

$$\begin{aligned} &\langle \Psi_{\alpha,N}(\cdot;\theta), D_{N^2}^{-1} \|x\|^n D_{N^2} \Psi_{\beta,N}(\cdot;\theta) \rangle \\ &= \langle \Psi_{\alpha,N}(\cdot;\theta), D_{N^2}^{-1} \|x\|^n \chi_{\|x\| \leq r_0} D_{N^2} \Psi_{\beta,N}(\cdot;\theta) \rangle + \mathcal{O}(N^{-\infty}). \end{aligned} \tag{89}$$

It now follows from (89) and the representation (138) of the projector, suitably dilated, that we have the operator estimate

$$\Pi_N^0(\theta) D_{N^2}^{-1} \|x\|^n D_{N^2} \Pi_N^0(\theta) = \Pi_N^0(\theta) D_{N^2}^{-1} \|x\|^n \chi_{\|x\| \leq r_0} D_{N^2} \Pi_N^0(\theta) + \Pi_N^0(\theta) R_N \Pi_N^0(\theta), \tag{90}$$

where the remainder R_N is given by

$$R_N \equiv \int_{\mathcal{A}} \int_{\mathcal{A}} \langle \Psi_{\alpha,N}(\cdot;\theta), D_{N^2}^{-1} \|x\|^n \chi_{\|x\|>r_0} D_{N^2} \Psi_{\beta,N}(\cdot;\theta) \rangle \; P_{\alpha,\beta} \; d\mu(\alpha) d\mu(\beta), \tag{91}$$

where $P_{\alpha,\beta}$ is the dyadic operator

$$P_{\alpha,\beta} \equiv \; |\Psi_{\alpha,N}(\theta)\rangle\langle\Psi_{\beta,N}(\theta)|. \tag{92}$$

To estimate $\|R_N\|$, we use estimate (88) and the fact that the measure μ on $\mathcal{A}$ is a probability measure. We obtain

$$\|R_N\| \leq C \sup_{\alpha,\beta\in\mathcal{A}} (\|\Psi_{\alpha,N}(\theta)\| \; \|\Psi_{\beta,N}(\theta)\|) e^{-Nc_4}, \tag{93}$$

where $c_4 > \log 240$ as in (77). The L^2-norms of the dilated coherent states can be estimates using (80) and (81). They satisfy the bound

$$\|\Psi_{\alpha,N}(\theta)\| \leq CN^2 e^{N(\log 10)/2}, \; |\Im\theta| < \pi/2. \tag{94}$$

Consequently, it follows from (93) and (94) that $\|R_N\| \leq C^{-Nc_5}$, for some $c_5 > 0$. Equation (71) then follows from (90), (93), and the fact that the measure μ on $\mathcal{A}$ is a probability measure
5. We can now prove the lemma. Recall from (34) that

$$W_h(F,\theta) = h^4 \epsilon(h) e^{\theta} F x_1 = h^2 \epsilon(h) D_{N^2}^{-1} (F x_1) D_{N^2}, \tag{95}$$

for $N = 1/h$. For part (1), we have

$$\|\Pi_N^0(\theta) W_h(F,\theta) \Pi_N^0(\theta)\| \leq c_0 (h^2 \epsilon(h)) F r_0 + \mathcal{O}(N^{-\infty}), \tag{96}$$

for a constant $r_0 > 1$. For part (2), we use $\|(\Pi_N^0(\theta) W_h(F,\theta))^* (W_h(F,\theta)\Pi_N^0(\theta))\| = \|W_h(F,\theta)\Pi_N^0(\theta)\|^2 = \|\Pi_N^0(\theta) W_h(F,\theta)\|^2$, so that estimate (90) with $n = 2$ provides the estimate. □

4.4. **Step 4. Reduction of the perturbation.** We now turn to controlling the operators $P_N(\theta)(S_h(F,\theta) - \tilde{E}_N) P_N(\theta)$ and $P_N(\theta)(S_h(F,\theta) - \tilde{E}_N)\Pi_N^0(\theta)$. Using Lemmas 2 and 3, we can prove the analog of [8, Lemma 5].

Lemma 4. *For any positive integer m, we have*

$$\Pi_N^0(\theta) \left(\frac{S_h(F,\theta) - \tilde{E}_N}{\epsilon(h) h^2} \right)^m P_N(\theta) = (\Pi_N^0(\theta) \tilde{W}_h(F,\theta) \Pi_N^0(\theta))^m P_N(\theta) + \Pi_N^0(\theta) R_{m,N}, \tag{97}$$

where $\|R_{m,N}\| = \mathcal{O}(N^{-\beta})$, for some $\beta > 0$, independent of m, and $\tilde{W}_h(F,\theta) = e^{i\theta} h^2 F x_1$, with $\theta \in \mathbb{R}$ and $0 < |\theta| < \pi/4$.

Proof. 1. To simplify notation, we suppress the θ in the notation. We begin with a simple identity:

$$\Pi_N^0 (S_h - \tilde{E}_N) P_N = \Pi_N^0 (S_h - \tilde{E}_N) \Pi_N^0 P_N + \Pi_N^0 (S_h - \tilde{E}_N)(\Pi_N^0)^{\perp} P_N. \tag{98}$$

We need an identity that follows from analyticity. Since $\tilde{E}_N$ remains an eigenvalue of the dilated hydrogen atom Hamiltonian, $H_V(\theta)$, we have

$$\Pi_N^0(\theta)(H_V(\theta) - \tilde{E}_N)\Pi_N^0(\theta) = 0. \tag{99}$$

Using this (99), and the fact that $\Pi_N^0 H_V(\Pi_N^0)^\perp = 0$, we have

$$\Pi_N^0(S_h - \tilde{E}_N)\Pi_N^0 = \Pi_N^0 W_h \Pi_N^0 \quad (100)$$

$$\Pi_N^0(S_h - \tilde{E}_N)(\Pi_N^0)^\perp = \Pi_N^0 W_h (\Pi_N^0)^\perp. \quad (101)$$

Substituting these into (98), we obtain

$$\Pi_N^0(S_h - \tilde{E}_N)P_N = \Pi_N^0 W_h \Pi_N^0 P_N + \Pi_N^0 W_h (\Pi_N^0)^\perp P_N. \quad (102)$$

2. To estimate the second term on the right in (102), we use part (1) of Lemma 2 and part (2) of Lemma 3:

$$\|\Pi_N^0 W_h (\Pi_N^0)^\perp P_N\| \leq \|\Pi_N^0 W_h\| \; \|(\Pi_N^0)^\perp P_N\| = \mathcal{O}(N^{4-2K-\delta}). \quad (103)$$

We take the m^{th} power of (102) and, because of (103), we have

$$(\Pi_N^0(S_h - \tilde{E}_N)P_N)^m = (\Pi_N W_h \Pi_N^0 P_N)^m + \Pi_N^0 \tilde{R}_{m,N}, \quad (104)$$

where the error term $\tilde{R}_{m,N}$ has the form

$$\tilde{R}_{m,N} = \sum_{\ell=1}^{m} \begin{pmatrix} m \\ \ell \end{pmatrix} \|\Pi_N^0 W_h \Pi_N^0 P_N\|^{m-\ell} \|\Pi_N^0 W_h (\Pi_N^0)^\perp P_N\|^\ell, \quad (105)$$

From Lemma 2 part (1) and Lemma 3, we obtain

$$\|\Pi_N^0 W_h \Pi_N^0 P_N\|^{m-\ell} \|\Pi_N^0 W_h (\Pi_N^0)^\perp P_N\|^\ell \leq C(\theta)(\epsilon(h)h^2)^m \mathcal{O}(N^{-\delta}). \quad (106)$$

Consequently, $\tilde{R}_{m,N}$ satisfies the estimate

$$\|\tilde{R}_{m,N}\| \leq (\epsilon(h)h^2)^m \mathcal{O}(N^{-\delta}). \quad (107)$$

3. We next prove that

$$(\Pi_N^0 W_h \Pi_N^0 P_N)^m = (\Pi_N^0 W_h \Pi_N^0)^m P_N + \Pi_N^0 K((\epsilon(h)h^2)^m \mathcal{O}(N^{-\delta})), \quad (108)$$

for all $m \in \mathbb{N}$ by induction on m, where we use the notation K introduced before Lemma 3. We proceed by induction. Equality (108) is trivially true for $m = 1$. We assume it is true for $m - 1$ and verify it for m. We write

$$\begin{aligned}(\Pi_N^0 W_h \Pi_N^0 P_N)^m &= (\Pi_N^0 W_h \Pi_N^0 P_N)(\Pi_N^0 W_h \Pi_N^0 P_N)^{m-1} \\ &= (\Pi_N^0 W_h \Pi_N^0 - \Pi_N^0 W_h \Pi_N^0 P_N^\perp)[(\Pi_N^0 W_h \Pi_N^0)^{m-1} P_N \\ &\quad + \Pi_N^0 K((h^2\epsilon(h))^{m-1}\mathcal{O}(N^{-\delta}))] \\ &= (\Pi_N^0 W_h \Pi_N^0)^m P_N + (\Pi_N^0 W_h \Pi_N^0) K((h^2\epsilon(h))^{m-1}\mathcal{O}(N^{-\delta})) \\ &\quad - \Pi_N^0 W_h \Pi_N^0 P_N^\perp (\Pi_N^0 W_h \Pi_N^0)^{m-1} P_N \\ &\quad - \Pi_N^0 W_h \Pi_N P_N^\perp \Pi_N^0 K((h^2\epsilon(h))^{m-1}\mathcal{O}(N^{-\delta})). \end{aligned} \quad (109)$$

Using the estimates in Lemma 3 for $\Pi_N^0 W_h \Pi_N^0$, we establish (108).

4. We next prove a similar estimate

$$(\Pi_N^0(S_h - \tilde{E}_N)P_N)^m = \Pi_N^0(S_h - \tilde{E}_N)^m P_N + \Pi_N^0(\epsilon(h)h^2)^m \mathcal{O}(N^{-\delta}). \quad (110)$$

In order to estimate the resonance term $(S_h - \tilde{E}_N)P_N$, we write

$$(S_h - \tilde{E}_N)P_N = (S_h - \tilde{E}_N)P_N(P_N - \Pi_N^0) + P_N W_h \Pi_N^0. \quad (111)$$

Noting that $\|\Pi_N^0 - P_N\| < 1$, we have from (111),

$$P_N(S_h - \tilde{E}_N)P_N = P_N W_h \Pi_N^0 (1 + (\Pi_N^0 - P_N))^{-1}. \quad (112)$$

From Lemma 2, we obtain the estimate

$$\|(S_h - \tilde{E}_N)P_N\| \leq c_0 h^2 \epsilon(h). \tag{113}$$

Given estimate (113), we prove (110) by induction. Assuming (110) for $m-1$, we write

$$\begin{aligned}
&(\Pi_N^0(S_h - \tilde{E}_N)P_N)^m - \Pi_N^0(S_h - \tilde{E}_N)^m P_N \\
&= \Pi_N^0(S_h - \tilde{E}_N)\Big[P_N(\Pi_N^0(S_h - \tilde{E}_N)P_N)^{m-1} - \\
&\quad -(S_h - \tilde{E}_N)^{m-1}P_N\Big]
\end{aligned} \tag{114}$$

From (113), we have the bound

$$\|(S_h - \tilde{E}_N)^{m-1}P_N\| \leq \|[(S_h - \tilde{E}_N)P_N]^{m-1}\| \leq (c_0 h^2 \epsilon(h))^{m-1}. \tag{115}$$

Consequently, the norm of the left side of (114) may be bounded above by

$$\|\Pi_N^0(S_h - \tilde{E}_N)P_N[-P_N(\Pi_N^0)^\perp(S_h - \tilde{E}_N)^{m-1}P_N + P_N\Pi_N^0 K((h^2\epsilon(h))^{m-1}\mathcal{O}(N^{-\delta}))]\|. \tag{116}$$

The estimate (110) for m now follows from this and (113) and (115). This completes the proof of Lemma 4 □

4.5. **Completion of the proof of Theorem 4.** In order to estimate the trace of $(S_h(F) - \tilde{E}_N)^m P_N$ on the left side in (39), we write

$$(S_h(F) - \tilde{E}_N)^m P_N = \Pi_N^0(S_h(F) - \tilde{E}_N)^m P_N + (\Pi_N^0)^\perp(S_h(F) - \tilde{E}_N)^m P_N. \tag{117}$$

Due to Lemma 4, we have

$$\begin{aligned}
(S_h(F) - \tilde{E}_N)^m P_N - (\Pi_N^0 W_h(F)\Pi_N^0)^m &= (\Pi_N^0)^\perp(S_h(F) - \tilde{E}_N)^m P_N \\
&\quad + (\epsilon(h)h^2)^m \Pi_N^0 R_{m,N} \\
&\quad - (\Pi_N^0 W_h(F)\Pi_N^0)^m P_N^\perp.
\end{aligned} \tag{118}$$

We estimate the trace norm of each term on the right in (118).

For the first term, we use the fact that $\|P_N\|_1 = d_N$, part (1) of Lemma 2, and estimates on resonances in order to estimate $\|(S_h(F) - \tilde{E}_N)^m P_N\|$ as N^{-1}, and we obtain

$$\begin{aligned}
\|(\Pi_N^0)^\perp(S_h(F) - \tilde{E}_N)^m P_N\|_1 &\leq \|(\Pi_N^0)^\perp P_N\|\|P_N\|_1\|(S_h(F) - \tilde{E}_N)^m P_N\| \\
&\leq d_N N^{-\alpha-1}.
\end{aligned} \tag{119}$$

For the second term on the right in (118), we have

$$\begin{aligned}
\|(\epsilon(h)h^2)^m \Pi_N^0 R_{m,N}\|_1 &\leq (\epsilon(h)h^2)^m \|\Pi_N^0\|_1 \|R_{m,N}\| \\
&\leq d_N(\epsilon(h)h^2)^m \|R_{m,N}\|.
\end{aligned} \tag{120}$$

The third term is estimated as

$$\begin{aligned}
\|(\Pi_N^0 W_h(F)\Pi_N^0)^m P_N^\perp\|_1 &\leq \|\Pi_N^0\|_1 \|(\Pi_N^0 W_h(F)\Pi_N^0)^m\| \|\Pi_N^0 P_N^\perp\| \\
&\leq d_N(\epsilon(h)h^2)^m N^{-\alpha}.
\end{aligned} \tag{121}$$

Finally, we write

$$\begin{aligned} Tr((S_h(F)-\tilde{E}_N)^m P_N) &= Tr(\Pi_N^0 W_h(F)\Pi_N^0)^m \\ &\quad + Tr\{(S_h(F)-\tilde{E}_N)^m P_N - (\Pi_N^0 W_h(F)\Pi_N^0)^m\} \end{aligned} \tag{122}$$

with

$$\begin{aligned} &|Tr\{(S_h(F)-\tilde{E}_N)^m P_N - (\Pi_N^0 W_h(F)\Pi_N^0)^m\}| \\ &\leq \|(S_h(F)-\tilde{E}_N)^m P_N - (\Pi_N^0 W_h(F)\Pi_N^0)^m\|_1 \\ &\leq d_N(\epsilon(h)h^2)^m N^{-\alpha}. \end{aligned} \tag{123}$$

Finally, restoring the complex parameter θ, we analyze the function

$$\xi(\theta) \equiv Tr((\Pi_N^0(\theta)W_h(F,\theta)\Pi_N^0(\theta))^m). \tag{124}$$

For $\theta \in \mathbb{R}$, we have,

$$\begin{aligned} \xi(\theta) &= Tr(D_{exp(\theta)}(\Pi_N^0 W_h(F)\Pi_N^0)^m D_{exp(-\theta)}) \\ &= Tr((\Pi_N^0 W_h(F)\Pi_N^0)^m). \end{aligned} \tag{125}$$

The function $\theta \to \xi(\theta)$ is analytic in a neighborhood of the real axis and independent of θ on the real axis, and is thus constant. Hence we can write

$$Tr((S_h(F,\theta)-\tilde{E}_N)^m P_N(\theta)) = Tr((\Pi_N^0 W_h(F)\Pi_N^0)^m) + E_{m,N}(\theta), \tag{126}$$

where $E_{m,N}(\theta) = \mathcal{O}((\epsilon(h)h^2)^m N^{-\alpha})$. This completes the proof of Theorem 4.

5. Trace estimate for the Stark perturbation of the hydrogen atom

The next step in the proof of Theorem 1 consists of evaluating the trace on the right side of (36). Let $\tilde{W}_h(F) = h^2 F x_1$. The sum on the right side of (36) is

$$\frac{1}{d_N}\sum_{i=1}^{d_N}\left(\frac{\tau_{N,i}}{h^2\epsilon(h)}\right)^m = \frac{1}{d_N}Tr((\Pi_N^0\tilde{W}_h(f)\Pi_N^0)^m). \tag{127}$$

note that $\tilde{W}_h(F) = W_h(F)/(h^2\epsilon(h))$. Since $\tilde{W}_h(F)$ is a polynomially-bounded perturbation, we use a general result of Thomas-Villegas-Blas [7, Theorem 4.2] in order to evaluate the semiclassical limit of the expression on the right in (127) as $N \to \infty$.

5.1. Polynomially-bounded perturbations.

The main result of [7, Theorem 4.2] on the semiclassical limit for polynomially bounded perturbations is the following theorem. We slightly change notation from [7] and write $h = 1/N$ and $k = N$.

Theorem 5. [7, Theorem 4.2] *Let V be a polynomially bounded, continuous function on $\mathbb{R}^3$ and let $g : \mathbb{R} \to \mathbb{R}$ be continuous. Then, we have*

$$\lim_{N\to\infty}\frac{1}{N^2}Tr(\Pi_N^0 g(\Pi_N^0 D_{N^{-2}} V D_{N^2}\Pi_N^0)) = \int_{\alpha\in\mathcal{A}} g\left(\frac{1}{2\pi}\int_0^{2\pi} V(x(t,\alpha))\ dt\right) d\mu(\alpha). \tag{128}$$

We remark that when V is a polynomial, as in our case, the proof of Theorem 5 is easier. In order to apply this result to (127), we take $g(s) = s^m$ and $V(x) = Fx_1$. Then we have from (6) that $(D_{N^2}^{-1} V D_{N^2})(x) = \tilde{W}_h(F)(x)$ with $h = 1/N$.

Using the decomposition of the projector Π_N^0 into coherent states (138), the trace on the left in (128), with $g(s) = s^m$, may be expressed as an m-fold multiple integral with respect to $\alpha_j \in \mathcal{A}$ of matrix elements, in the momentum representation, given by

$$(i/N)\langle J^{1/2} K \Phi_{\alpha_i,N}, (F\nabla_{p_1}) J^{1/2} K \Phi_{\alpha_{i+1},N}\rangle, \tag{129}$$

where $\Phi_{\alpha,N}$ is the function of $\mathbb{S}^3$ defined in (133). Lemma 4.3 of [7] states that for any $\delta > 0$, the matrix element in (129) is given by

$$(i/N)\langle J^{1/2} K \Phi_{\alpha_i,N}, J^{1/2} K \Phi_{\alpha_{i+1},N}\rangle \left(\frac{1}{2\pi} \int_0^{2\pi} F\ x(t,\alpha_i)_1\ dt + \mathcal{O}(N^{\delta-1/2}) \right) + \mathcal{O}(N^{-\infty}), \tag{130}$$

where $x(t,\beta)_1$ is the first component of the vector $x(t,\beta) \in \mathbb{R}^3$. This vector and a corresponding momentum vector $p(t,\beta)$, form a solution to Hamilton's equations for motion for the Hamiltonian $h(x,p) = (1/2)p^2 - |x|^{-1}$ with energy $-1/2$. The parameter $\beta \in \mathcal{A}$ labels the Kepler orbit with energy $-1/2$. In the limit as $N \to \infty$, the matrix elements approach zero unless $\alpha_i = \alpha_{i-1}$. This reduces the multiple m-fold integral to a single integral over $\mathcal{A}$ of the m^{th}-power of the integral in (130).

5.2. **Conclusion of the proof of Theorem 1.** We have now proved the following result. For $\epsilon(h) = h^{6+\delta}$, with $0 < \delta < 1$ and $h = 1/N$, the resonance shifts $z_{N,i}(F, 1/N)$ satisfy, for any $m \in \mathbb{N}$, the limit

$$\lim_{N\to\infty} \sum_{j=1}^{d_N} \left(\frac{z_{N,i}(F,1/N) - E_N(1/N)}{\epsilon(1/N)} \right)^m = \int_{\alpha\in\mathcal{A}} \left(\frac{1}{2\pi} \int_0^{2\pi} [Fx(t,\alpha)_1]\ dt \right)^m d\mu(\alpha). \tag{131}$$

To finish the proof of Theorem 1, two steps remain to be done. First, we rewrite the integral over $\mathcal{A}$ on the right in (131) in terms of the integral over the energy surface $\Sigma(-1/2)$. Second, we show how to replace the monomial s^m by a function ρ that is analytic in a fixed disk about the origin.

As for the first task, we refer to [8, pages 141-142]. It is noted there that the push-forward of the measure μ on $\mathcal{A}$ is the Liouville measure μ_L on the energy surface $\Sigma(-1/2)$. Furthermore, the Kepler orbit corresponds to the Kepler flow $\tilde{\phi}_t(x,p)$ on this energy surface.

As for the second task, the function ρ of Theorem 1 is analytic in a disk of radius $3F$ about the origin. Since the perturbation $F \cdot (\tilde{\phi}_t(x,p))_1$ is bounded by $2F$ for orbits $\tilde{\phi}_t$ on the energy surface $\Sigma(-1/2)$, the estimate (131) guarantees convergence in the trace of the power series expansion for ρ. This concludes the proof of Theorem 1.

6. Appendix 1: Coherent states for the hydrogen atom

We review the construction and properties of the coherent states that form an overcomplete set in the eigenspace $\mathcal{E}_\ell$ of the hydrogen atom Hamiltonian corresponding to the eigenvalue $E_\ell = -1/(2h^2\ell^2)$. Let $\mathcal{A}$ be the five real-dimensional subspace of $\mathbb{C}^4$ defined by

$$\mathcal{A} = \{\alpha = (\alpha_1, \alpha_2, \alpha_3, \alpha_4) \mid \alpha_j \in \mathbb{C},\ \|\Re\alpha_j\| = \|\Im\alpha_j\| = 1,\ \Re\alpha \cdot \Im\alpha = 0\}. \quad (132)$$

This provides a parametrization of the co-sphere bundle $S^*\mathbb{S}^3$ of the three-sphere. There is a $SO(4)$-rotationally invariant probability measure on $\mathcal{A}$ that we denote by μ. Coherent states on $\mathbb{S}^3$ have the form

$$\Phi_{\alpha,\ell}(\omega) = a(\ell)(\alpha \cdot \omega)^\ell,\ \omega \in \mathbb{S}^3,\ \alpha \in \mathcal{A},\ \ell \in 0, 1, 2, \ldots. \quad (133)$$

The coefficient $a(\ell) \sim \ell^{1/2}$ is fixed by the requirement that the $L^2(\mathbb{S}^3)$-norm of $\Phi_{\alpha,N}$ is equal to one, see [7, (2.11)]. These states are hyper-spherical harmonics. They are eigenstates of the spherical Laplacian $-\Delta_{\mathbb{S}^3}$ with eigenvalue $\ell(\ell+2)$. The entire family $\{\Phi_{\alpha,\ell}(\omega) \mid \alpha \in \mathcal{A}\}$ is over complete and spans the eigenspace of $-\Delta_{\mathbb{S}^3}$ with eigenvalue $\ell(\ell+2)$. We note that these states have the property that as $N \to \infty$ they concentrate on the great circle $\{\omega \in \mathbb{S}^3 \mid |\alpha \cdot \omega| = 1\}$ generated by the real and imaginary parts of α.

In momentum space $\mathbb{R}^3$, the coherent states have the following form. The inverse of the stereographic projection from the three sphere $\mathbb{S}^3$ to $\mathbb{R}^3$ is the mapping $p \in \mathbb{R}^3 \to \omega(p) \in \mathbb{S}^3$ defined by

$$\begin{aligned} \omega_j(p) &= \frac{2p_j}{\|p\|^2 + 1},\ j = 1, 2, 3 \\ \omega_4(p) &= \frac{\|p\|^2 - 1}{\|p\|^2 + 1}. \end{aligned} \quad (134)$$

For any $\alpha \in \mathcal{A}$, we define

$$\hat{\Psi}_{\alpha,\ell}(p) = a(\ell-1)\ell^{3/2} \left(\frac{2}{\ell^2\|p\|^2 + 1} \right)^2 (\alpha \cdot \omega(\ell p))^{\ell-1},\ p \in \mathbb{R}^3. \quad (135)$$

These functions are in $L^2(\mathbb{R}^3)$. Their Fourier transforms are eigenfunctions of H_V with eigenvalue E_ℓ [1, section II.B]. They form an overdetermined basis of the ℓ^2-dimensional eigenspace $\mathcal{E}_\ell \subset L^2(\mathbb{R}^3)$ in the momentum space representation.

For $\theta \in \mathbb{R}$, we scale these momentum space functions by e^θ to obtain

$$\hat{\Psi}_{\alpha,\ell}(e^\theta p) = a(\ell-1)\ell^{3/2} \left(\frac{2}{\ell^2 e^{2\theta}\|p\|^2 + 1} \right)^2 (\alpha \cdot \omega(\ell e^\theta p))^{\ell-1},\ p \in \mathbb{R}^3. \quad (136)$$

These functions are analytic L^2-valued functions for $|\Im\theta| < \pi/2$.

The configuration space coherent states are obtained by the inverse Fourier transform:

$$\begin{aligned}\Psi_{\alpha,\ell}(x) &= \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} d^3p \; e^{ix\cdot p} \; \hat{\Psi}_{\alpha,\ell}(p) \\ &= \frac{a(\ell-1)\ell^{3/2}}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} d^3p \; e^{ix\cdot p} \; \left(\frac{2}{\ell^2\|p\|^2+1} \right)^2 (\alpha \cdot \omega(\ell p))^{\ell-1}.\end{aligned} \tag{137}$$

These form an overdetermined basis of normalized (but not orthogonal) L^2-functions for $\mathcal{E}_\ell \subset L^2(\mathbb{R}^3)$ in the configuration space picture. Let μ be the probability measure on $\mathcal{A}$. The orthogonal projector Π_ℓ^0 onto the eigenspace $\mathcal{E}_\ell$ may be written as

$$\Pi_\ell^0 = \ell^2 \int_{\mathcal{A}} |\Psi_{\alpha,\ell}\rangle\langle\Psi_{\alpha,\ell}| \; d\mu(\alpha). \tag{138}$$

For $\theta \in \mathbb{R}$, the dilated coherent states are

$$\begin{aligned}\Psi_{\alpha,\ell}(x;\theta) &\equiv D_{exp(\theta)}\Psi_{\alpha,\ell}(x) = e^{3\theta/2}\Psi_{\alpha,\ell}(e^\theta x) \\ &= \frac{e^{-3\theta/2}}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} d^3p \; e^{ix\cdot p} \; \hat{\Psi}_{\alpha,\ell}(e^{-\theta}p) \\ &= a(\ell-1)\ell^{3/2} \frac{e^{-3\theta/2}}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} d^3p \; e^{ix\cdot p} \left(\frac{2}{\ell^2 e^{-2\theta}\|p\|^2+1} \right)^2 (\alpha \cdot \omega(\ell e^{-\theta}p))^{\ell-1}.\end{aligned} \tag{139}$$

From the comments after (136), it follows that $\Psi_{\alpha,\ell}(x;\theta)$ has an analytic continuation as an L^2-valued function of θ for $|\Im\theta| < \pi/2$. We also consider the dilated projector $\Pi_\ell^0(\theta) = D_{exp(\theta)}\Pi_\ell^0 D_{exp(-\theta)}$. We extend these dilated operators to $\theta \in \mathbb{C}$ provided $|\Im\theta| < \pi/2$. As mentioned above, the coherent states concentrate on the Kepler orbit as $\ell \to \infty$. Lemma 3 is a consequence of this fact.

7. Appendix 2: Moments of the hydrogen atom eigenfunctions

We give the brief proof of the localization property of the eigenstates of the hydrogen atom Hamiltonian discussed in section 4.3. The eigenfunctions of H_V may be written as $\psi_{n\ell m}(r,\tilde{\theta},\phi) = e^{-r/n}F_{nl}(r)Y_{lm}(\tilde{\theta},\phi)$, with $n = 1, 2, \ldots$, the principal quantum number. The functions $Y_{\ell m}$ are the spherical harmonics (ℓ, m) labeling the angular momentum so that $0 \leq \ell \leq n-1$ and $-\ell \leq m \leq \ell$. The radial component $F_{nl}(r) = A_{n\ell}(2r/n)^\ell L_{n-\ell-1}^{2\ell+1}(2r/n)$, where $L_{n-\ell-1}^{2\ell+1}(r)$ is the associated Laguerre polynomial of degree $n-\ell-1$. The normalization constant is $A_{n\ell} = (2/n^2)\sqrt{(n-\ell-1)!/[(n+\ell)!]^3}$. The dilated eigenfunctions $\psi_{n\ell m}(\theta)(r) \equiv (D_{exp(\theta)}\psi_{n\ell m})(r) = e^{3\theta/2}\psi_{n\ell m}(e^\theta r)$ are analytic L^2-valued functions in the strip $|\Im\theta| < \pi/2$. Consequently, the function $f(\theta) \equiv \langle\psi_{n\ell m}(\theta), \|x\|^k\psi_{n\ell' m'}(\theta)\rangle$ is analytic on the strip $|\Im\theta| < \pi/2$. For $\theta \in \mathbb{R}$, we have $f(\theta) = e^{-k\theta}f(0)$. The function $\tilde{f}(\theta) = e^{-k\theta}f(0)$ is an entire analytic function. By the identity principle for analytic functions, we have $\tilde{f}(\theta) = f(\theta)$ on the strip $|\Im\theta| < \pi/2$.

We first want to estimate the large n behavior of the expectation of powers of the position operator in the dilated eigenstates $\psi_{n\ell m}$ as in (68). Since $f(\theta) = e^{-m\theta} f(0)$, this reduces to an estimate on moments of the position operator. For any $k > -2\ell - 1$, these moments are well-known and computed in section 3, Appendix B of Messiah [6]. Let

$$\langle \|x\|^k \rangle_{n\ell m} \equiv \langle \psi_{n\ell m}(\theta), \|x\|^k \psi_{n\ell' m'}(\theta) \rangle. \tag{140}$$

Note that because of the spherical symmetry, the quantum numbers (ℓ, m) must be the same in (140). Properties of the Laguerre polynomials leads to

$$\langle \|x\| \rangle_{n\ell m} = \frac{1}{2}[3n^2 - \ell(\ell+1)], \tag{141}$$

and a recursion formula for higher moments $k \geq 2$:

$$\langle \|x\|^k \rangle_{n\ell m} = n^2 \frac{2k+1}{k+1} \langle \|x\|^{k-1} \rangle_{n\ell m} - \frac{n^2 k}{4(k+1)} [(2\ell+1)^2 - k^2] \langle \|x\|^{k-2} \rangle_{n\ell m}. \tag{142}$$

It is easy to verify from (141) and (142) that

$$\langle \psi_{n\ell m}, \|x\|^k \psi_{n\ell m}(\theta) \rangle = \mathcal{O}(n^{2k}), \tag{143}$$

since $0 \leq l \leq n-1$ (see [6, section B.3]), verifying (68).

Secondly, we want to compute the matrix elements of the Stark perturbation. It is easier to do the calculation with the electric field in the three direction x_3 because of the properties of the usual spherical harmonics. The result is independent of the field direction so we assume this here. Recalling the identity principle for analytic functions used above, the matrix element of the Stark perturbation is

$$\begin{aligned} \langle \psi_{n\ell m}(\theta), W_h(F,\theta) \psi_{n\ell' m'}(\theta) \rangle &= \epsilon(h) h^2 e^\theta F \langle \psi_{n\ell m}(\theta), x_3 \psi_{n\ell' m'}(\theta) \rangle \\ &= \epsilon(h) h^2 F \langle \psi_{n\ell m}, x_3 \psi_{n\ell' m'} \rangle, \ |\Im\theta| < \pi/2. \end{aligned} \tag{144}$$

We write $x_3 = r\cos\tilde{\theta}$, where $\tilde{\theta}$ is the angle with the x_3-axis. By the Cauchy-Schwarz inequality and the first moment estimate (141), we have

$$|\langle \psi_{n\ell m}, x_3 \psi_{n\ell' m'} \rangle| \leq \|r^{1/2} \psi_{n\ell' m'}\| \ \|r^{1/2} \psi_{n\ell m}\| = \mathcal{O}(n^2), \tag{145}$$

since $0 \leq l \leq n-1$ (see [6, section B.3].)

8. Appendix 3: The quadratic estimate

We restate the quadratic estimate appearing in Proposition II.4 of [4]. In the notation of that paper, let $h(\alpha) = -\Delta + \alpha x_1$ where $|\Im\alpha| > 0$. Let $\theta = \arg\alpha$ and define two constants

$$c(\alpha) = (3/2)(1 - |\cos\theta|)^{3/2} |\sin\theta|^{3/2} |\alpha|^{4/3}, \ \beta(\alpha) = (1 - |\cos\theta|)/2. \tag{146}$$

then, for all $\psi \in S(R^3)$, we have

$$\|h(\alpha)\psi\|^2 + c(\alpha)\|\psi\|^2 \geq \beta(\alpha)(\|\Delta\psi\|^2 + \|x_1\psi\|^2). \tag{147}$$

In our case, we have

$$H_0(h, F, \theta) = e^{-2i\theta}[-\Delta + e^{3i\theta} h^4 \epsilon(h) F x_1] = e^{-2i\theta} h(\tilde{\alpha}), \tag{148}$$

where $\tilde{\alpha} = e^{3i\theta} h^4 \epsilon(h) F$. From (146), we find that

$$c(\tilde{\alpha}) = \mathcal{O}(N^{-(4/3)(4+K+\delta)}), \ \beta(\tilde{\alpha}) = \mathcal{O}(1). \tag{149}$$

Consequently, we have the following bound for $z \in \gamma_N$:

$$\|x_1(H_0(h, F, \theta) - z)^{-1}\| = \mathcal{O}(1). \tag{150}$$

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Department of Mathematics, University of Kentucky, Lexington, Kentucky 40506-0027, USA

E-mail address: hislop@ms.uky.edu

Universidad Nacional Autónoma de México, Instituto de Matemáticas, Unidad Cuernavaca, Mexico

E-mail address: villegas@matcuer.unam.mx