ABSENCE OF A SCOTT CORRECTION FOR THE TOTAL BINDING ENERGY OF NONINTERACTING FERMIONS IN A SMOOTH POTENTIAL WELL

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This thesis is dedicated to the memory of my father,

Thomas Richard Huxtable, Jr., M.D.

There are questions which we could never get over if we were not delivered from them by the operation of nature.

Reflections on Sin, Pain,
Hope, and the True Way
Franz Kafka

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ABSTRACT

It is shown, for V in a particular class of smooth functions, that the total binding energy, $E(Z)$, of Z noninteracting Fermions in the potential well $Z^{4/3}V(Z^{1/3}x)$, obeys $E(Z) = c_{TF}(V)Z^{7/3} + 0(Z^{5/3})$ as $Z \to \infty$. Here $c_{TF}(V)$ is the coefficient predicted by the Thomas-Fermi theory. This result is consistent with the conjectured Scott correction, which occurs at order Z^2, to the total binding energy of an atom of atomic number Z. This correction is thought to arise only because $V(x) \sim -|x|^{-1}$ near $x = 0$ in the atomic problem, and so V is *not* a smooth function.

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CHAPTER I

Introduction

Since the advent of the quantum theory, there have been efforts made to apply the theory to increasingly more complicated physical systems. This has, more often than not, made necessary the invention of various approximation schemes. One of the earliest of these is now generally known as the Thomas-Fermi theory, and one of its first uses was in the study of large atoms [24].

For an atom with Z electrons, an infinite mass, point nucleus of charge Z, and neglecting relativistic effects, we have the quantum mechanical Hamiltonian or Schrödinger operator

$$H(Z) = \sum_{i=1}^{Z} \left(-\Delta_i - \frac{Z}{|x_i|}\right) + \sum_{1 \leq i < j \leq Z} |x_i - x_j|^{-1}. \tag{1.1}$$

We consider this Hamiltonian over antisymmetric wave functions in $\bigwedge_{i=1}^{Z} L^2(\mathbb{R}^3;\mathbb{C}^2)$ and denote by $E(Z)$ the ground state energy of $H(Z)$. (Our units are such that $m = \frac{1}{2}$, $e = \hbar = 1$, so our energy unit below is $\frac{me^4}{\hbar^2} \doteq 54.4$ eV.) Milne [14] used the Thomas-Fermi theory to show that

$$E(Z) \simeq cZ^{7/3} \text{ with } c = c_{\text{Milne}} = -.308. \tag{1.2}$$

(This value of c was a little low due to inaccuracies in the numerical solution of the Thomas-Fermi differential equation ([24], Equation 1.3). The correct value is $c_{TF} = -.3844$.) Using spectroscopic data to find $E(Z)$ for

$Z = 2,3,\ldots,9$, Young [25] found that the observed values obeyed

$$E(Z) \simeq c_{\text{Young}} \; Z^{7/3 \pm 1/1000} \quad \text{for } 2 \leq Z \leq 9$$

and $c_{\text{Young}} = -.288$.

It was suspected by Young that the discrepancy between c_{Young} and c_{Milne} was due to the numerical difficulties in the evaluation of c_{Young}. (However, the correct value c_{TF} makes the discrepancy worse.)

The first improvement on the Thomas-Fermi model of the atom was proposed by Dirac [5], who took into account the effect of exchange. As noted in [19], this adds to (1.2) a term $-.111\, Z^{5/3}$, which does not improve the agreement with the observed values. Equation (1.2) was cast further into doubt by Foldy [6], who found, from the then recent Hartree calculations on the atom for several Z between 10 and 90, that apparently,

$$E(Z) \simeq -\tfrac{1}{4}\, Z^{12/5} \quad \text{for} \quad 10 \lesssim Z \lesssim 90 .$$

One is surprised by this because (1.2) was derived from the Thomas-Fermi theory, in which the statistical assumptions should hold better for large Z.

This situation was finally resolved by Scott [19], who proposed the following leading order behavior:

$$E(Z) \doteq c_{\text{TF}}\, Z^{7/3} + \tfrac{1}{4} Z^2 - .111\, Z^{5/3} . \tag{1.3}$$

The Z^2 term is called the Scott correction and arises as a result of the inability of the Thomas-Fermi theory to describe the electrons near the nucleus, where the nuclear Coulomb potential varies rapidly. The argument essentially consists of treating the inner electrons as if they were in Bohr orbits around a nucleus of charge Z and treating the outer electrons with the usual Thomas-Fermi theory. (This argument is done very nicely in [18].) This derivation suggests that the Scott correction is independent of the presence of electron-electron repulsion, since the inner electrons that contribute to the Scott correction are insensitive to the presence of the other electrons when Z is large. However, electron-electron repulsion does contribute to the $Z^{7/3}$ and $Z^{5/3}$ terms in (1.3). In [20] it is shown that numerical fits to Hartree-Fock calculations for various Z are in exceedingly good agreement with (1.3). (The $Z^{5/3}$ coefficient is actually $-.133$, because of corrections to the Thomas-Fermi theory other than exchange effects as discussed in [1].)

Lieb and Simon [13] give a mathematically rigorous justification of (1.2) (with $c = c_{TF}$) starting from (1.1), in effect proving that the Thomas-Fermi theory gives the correct leading-order behavior. Their proof extends easily to more general Schrödinger operators of the form

$$H(Z) = \sum_{i=1}^{Z} \left[-\Delta_i + Z^{4/3}\, V(Z^{1/3}x_i)\right] + \sum_{1\leq i<j\leq Z} |x_i - x_j|^{-1} \tag{1.4}$$

and shows that

$$E(Z) = c_{TF}(V)\, Z^{7/3} + o(Z^{7/3}) \text{ as } Z \to +\infty .$$

($V(x) = -|x|^{-1}$ in (1.4) gives (1.1).) Here $c_{TF}(V)$ is the coefficient one obtains by applying the Thomas-Fermi theory to (1.4) and computing $E(Z)$. As noted in [13], the proof used cannot be improved so that we could see the Scott term. The proof basically gives upper and lower bounds to $E(Z)$, and the method of constructing these bounds makes them differ at order $0(Z^2)$.

Proving that the Scott correction in the atomic binding energy is correct has remained a challenging open problem. It was shown by Lieb [12] that a modification of the Thomas-Fermi theory, known as the Thomas-Fermi-von Weizsäcker theory, does produce a Z^2 correction in the atomic binding energy. However, unlike the case of the Thomas-Fermi theory, there is no theorem that connects the Thomas-Fermi-von Weizsäcker theory to the real quantum problem. There is probably no such theorem because one cannot simultaneously get the Z^2 correction conjectured by Scott [19] and the electron density conjectured by Lieb [12]. Thirring [23] has produced a lower bound, which says

$$E(Z) \geq c_{TF} Z^{7/3} (1 + 0(Z^{-2/33}))$$

for the atomic problem. Siedentop and Weikard [22] have recently proven the upper bound

$$E(Z) \leq c_{TF} Z^{7/3} + \tfrac{1}{4} Z^2 + o(Z^2).$$

The problem treated in this thesis was originally motivated by the results of Bander [1], where it appeared, at least formally, that if V in (1.4) had no singularities and was smooth, then E(Z) would be of the form

(1.5) $$E(Z) = c_{TF}(V) Z^{7/3} + 0(Z^{5/3}),$$

and we would have no "Scott correction" or Z^2 contribution. In this thesis, we treat the case of noninteracting particles; that is, we drop the $|x_i - x_j|^{-1}$ terms in (1.4). Also, we consider smooth potentials in the class $\mathcal{V}$, namely, those $V \in C^\infty(\mathbb{R}^3)$, which obey

$$c|x|^2 \leq V(x) \leq C|x|^2,$$

$$|\vec{\nabla} V(x)| \leq c'|x|$$

for some $c, C, c' > 0$, and all higher derivatives of V are bounded everywhere in x. The main result of this thesis (Theorem 7 at the beginning of Chapter IV) is that, for the Hamiltonian

$$H(Z) = \sum_{i=1}^{Z} (-\Delta_i + Z^{4/3} V(Z^{1/3} x_i)),$$

the ground state energy $E(Z)$ is as in (1.5) when the Fermi level is not at a critical value of the potential. (The Fermi level is the energy of the highest occupied single particle state.) This result is of interest because it suggests that there would be no Scott correction in the atomic binding energy, except for the fact that the nuclear potential seen by the electrons has a singularity, which is consistent with Scott's intuitive argument.

In Chapter II we start by introducing some notation and then prove a fundamental result (Theorem 1) that tells us, in effect, the "right way" to approach our problem. Two examples are discussed along the way. In Chapter III we use some recent mathematical methods to prove some facts about two functions related to the spectrum of $-\Delta + Z^{4/3} V(Z^{1/3} x)$. The proofs are outlined in Chapter III, leaving many of the mathematical details to the Appendices. Finally, in Chapter IV we put the results of Chapters II and III together to obtain our desired result. We then discuss the reason for not allowing the Fermi level to be at a critical value of the potential, and possible extensions to smooth potentials other than those in the class $\mathcal{V}$. Finally, a formal calculation is given, suggesting what the Scott correction might be for certain singular potentials.

CHAPTER II

A Fundamental Result

As motivated in the Introduction, we are interested in the ground-state energy of the quantum mechanical Hamiltonian

$$(2.1) \qquad H(Z) = \sum_{i=1}^{Z} \left[-\Delta_i + Z^{4/3} V(Z^{1/3} x_i) \right]$$

over antisymmetric wave functions in $\bigwedge_{i=1}^{Z} L^2(\mathbb{R}^3;\ \mathbb{C}^q)$. We choose units so that $\hbar = 1$ and $m = \frac{1}{2}$. This ground-state energy is given by

$$E(Z) = \sum_{j=1}^{Z} e_j(Z),$$

where

$e_j(Z) = j^{th}$ eigenvalue (counting multiplicity) of $-\Delta + Z^{4/3} V(Z^{1/3} x)$ over $L^2(\mathbb{R}^3;\ \mathbb{C}^q)$.

By rescaling energy by $Z^{-4/3}$, and distance by $Z^{-1/3}$, and defining $h = Z^{-1/3}$, we obtain (tolerating a common abuse of notation)

$$Z^{-4/3} E(Z) = E(h),$$

where

$$(2.2) \qquad E(h) = \sum_{j=1}^{h^{-3}} e_j(h);$$

$$(2.3) \qquad e_j(h) = j^{th} \text{ eigenvalue (counting multiplicity) of } -h^2\Delta + V(x) \text{ over } L^2(\mathbb{R}^3;\ \mathbb{C}^q).$$

It must be stressed that $h = Z^{-1/3}$ is not related to $\hbar$, which is implicit in (2.1). We use this notation because it is traditional in the work of Chapter III and because $h \to 0$ is suggestive of a semiclassical connection, which will be seen later.

Whereas before, we were interested in the asymptotic form of $E(Z)$ as $Z \to \infty$, with this change of variables, we are now interested in the asymptotic form of $E(h)$ as $h \to 0$. From the discussion in the Introduction, we anticipate that

$$(2.4) \qquad E(h) = c_1 h^{-3} + c_2 h^{-2} + O(h^{-1}) \quad \text{as } h \to 0$$

where c_1, c_2 are constants depending on the potential V. It is the primary point of this thesis to show that for a class of smooth potentials there is no "Scott correction;" i.e., $c_2 = 0$ in (2.4).

Now we must introduce some notation. We only consider potentials V, whose positive and negative parts, V_+ and V_-, satisfy $V_+ \in L^2(\mathbb{R}^3)_{loc}$ and $V_- \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. For such potentials, the Hamiltonian

$$H = H_h = -h^2\Delta + V$$

is self-adjoint. (See [16], sections X.2 and X.4.) Let $e_j(h)$ be the eigenvalues (if any) of H_h as in (2.3). Make the definitions

$$(2.5) \qquad N_h(e) = \#\{j : e_j(h) \le e\} \equiv \text{the number of eigenvalues of } H_h \text{ that are } \le e;$$

$$(2.6) \qquad N_c(e) = \frac{q}{(2\pi)^3} \iint_{p^2+V(x)\le e} d^3x\, d^3p \equiv \frac{q}{6\pi^2} \int_{V(x)\le e} (e - V(x))^{3/2} d^3x .$$

We further restrict the potentials under consideration by requiring that there be $\mu_0 \in \mathbb{R}$ and $\epsilon > 0$ so that $N_c(\mu_0) = 1$ and $N_c(\mu_0+\epsilon) < +\infty$. This restriction on V says that H_h has at least $h^{-3}(=Z)$ eigenvalues at the bottom of its spectrum. (This is necessary for (2.2) to make sense, and physically it means that V is a deep enough well for (2.1) to bind Z particles.) To see this, note that $h^{-3}N_c(e)$ is the semiclassical estimate for $N_h(e)$, and it is known ([17], Section XIII.15) that

$$\lim_{h\downarrow 0} h^3 N_h(e) = N_c(e)$$

for $e \leq \mu_0 + \epsilon$. Since

$$N_h(\mu_0+\epsilon) = h^{-3}N_c(e)\,(1+o(h)) \quad \text{as } h \to 0$$

and $N_c(\mu_0+\epsilon) > N_c(\mu_0) = 1$, we have

$$N_h(\mu_0+\epsilon) > h^{-3}$$

for h sufficiently small.

Next, define

(2.7) $$\mu_h = \min\{e : N_h(e) \geq h^{-3}\} \equiv \text{Fermi level that results when the lowest } h^{-3} = Z \text{ energy states in the potential well are occupied,}$$

and

(2.8) $$\Psi_h(e) = \int_{-\infty}^{e} N_h(e')\,de'.$$

The need for Ψ_h will become apparent momentarily. Since $N_h(e)$ is right continuous and non-decreasing in e, it defines a measure on $\mathbb{R}$ and we have

$$E(h) := \sum_{j=1}^{h^{-3}} e_j(h)$$

$$= \int_{(-\infty,\mu_h]} e\,dN_h(e) - \left[N_h(\mu_h) - h^{-3}\right]\mu_h$$

(the second term may be thought of as a correction to the first term, which over-counts if $N_h(\mu_h) > h^{-3}$; this may happen if the Fermi level μ_h has a multiplicity greater than one)

$$= h^{-3}\mu_h - \int_{-\infty}^{\mu_h} N_h(e)\,de$$

$$= h^{-3}\mu_h - \Psi_h(\mu_h)$$

after an integration by parts. In deriving this result, we had in mind that $h^{-3} = Z =$ integer number of particles, but

(2.9) $$E(h) = h^{-3}\mu_h - \Psi_h(\mu_h)$$

makes sense for all $h > 0$, and we will henceforth take (2.9) as our definition of $E(h)$ for all $h > 0$.

To understand the motivation for the following theorem, it should be noted that $N_h(e) - h^{-3}N_c(e)$ may oscillate with increasing magnitude $\sim h^{-2}$ as $h \to 0$. (This will be the case in the two examples to be discussed after the theorem.) It might be expected that this behavior carries over to $E(h)$; that is, $E(h) - c_1 h^{-3}$ might oscillate with magnitude $\sim h^{-2}$ as $h \to 0$. Hence, there would be no $c_2 h^{-2}$ term in (2.4), which is the term of primary interest to us! The following theorem shows that the asymptotic form of $E(h)$ may be smoother than N_h as $h \to 0$, and motivates the study of the asymptotic form of Ψ_h for small h.

First, define $n(e,h)$ so that

(2.10) $$N_h(e) = h^{-3}N_c(e) + h^{-2}n(e,h).$$

This function $n(e,h)$ describes the error made in approximating $N_h(e)$ by $h^{-3}N_c(e)$.

__Theorem 1:__ Suppose there are $\mu_0 \in \mathbb{R}$ and ϵ, h_0, $n_{max} > 0$ such that:

(2.11) $N_c(\mu_0) = 1$,

(2.12) $N_c(\mu_0 + \epsilon) < +\infty$, and

(2.13) $|n(e,h)| < n_{max}$ for $|e - \mu_0| \leq \epsilon$, $h \in (0, h_0]$.

(2.14) Then $E(h) = \mu_0 h^{-3} - \Psi_h(\mu_0) + O(h^{-1})$ as $h \to 0$.

The following two examples illustrate Theorem 1, which is then proven next. The examples also show that Theorem 1 is optimal in the sense that one does not generally have smoother asymptotics on N_h as input, nor can one generally conclude smoother asymptotics on $E(h)$.

<u>Example 1</u> ("Bohr atom"): Let $V(x) = -|x|^{-1}$. The eigenvalues of $-h^2\Delta + V$ are then known to be

$$e_{n\ell ms}(h) = \frac{-1}{4h^2n^2}, \quad \begin{cases} n = 1, 2, 3, \ldots \\ \ell = 0, 1, \ldots, n-1 \\ m = -\ell, -\ell+1, \ldots, \ell \\ s = 1, 2, \ldots, q \end{cases}.$$

By direct computation, for $e < 0$

$$N_h(e) = \sum_{\substack{n=1,2,3,\cdots \\ n \le \frac{1}{2h\sqrt{-e}}}} \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} \sum_{s=1}^{q} 1 = \sum_{n=1}^{[\upsilon]} q n^2$$

$$= q\left\{\tfrac{1}{3}[\upsilon]^3 + \tfrac{1}{2}[\upsilon]^2 + \tfrac{1}{6}[\upsilon]\right\},$$

where $\upsilon = \frac{1}{2h\sqrt{-e}}$ and $[x]$ = greatest integer $\le x$. Define $\delta = \delta(e,h) = \upsilon - [\upsilon]$; then one finds

$$N_h(e) = h^{-3}N_c(e) + h^{-2}n(e,h),$$

where $N_c(e) = \frac{q}{24}(-e)^{-3/2}$ and $n(e,h) = q\left\{(\tfrac{1}{2} - \delta)\frac{1}{4(-e)} + (\tfrac{1}{6} - \delta + \delta^2)\frac{h}{2\sqrt{-e}} + (-\tfrac{\delta}{6} + \tfrac{\delta^2}{2} - \tfrac{\delta^3}{3})h^2\right\}$. Note that, since $0 \le \delta(e,h) < 1$, $|n(e,h)|$ is bounded for $h \in (0,h_0]$, $e < e_0$ where h_0 and $-e_0$ are any positive numbers.

By similar calculation, one finds

$$\Psi_h(e) = \sum_{n=1}^{[\upsilon]} qn^2\left(e - \frac{-1}{4h^2n^2}\right)$$

$$= \frac{q}{12h^3\sqrt{-e}} - \frac{q}{8h^2} + h^{-1}\psi(e,h),$$

where $|\psi(e,h)|$ is bounded for $h \in (0,h_0]$, $e < e_0$. The Theorem then gives, with $\mu_0 = -\left(\frac{q}{24}\right)^{2/3}$,

$$E(h) = -\frac{3^{1/3}q^{2/3}}{4} h^{-3} + \frac{q}{8}h^{-2} + 0(h^{-1}). \tag{2.15}$$

With $q = 2$ for electrons, we get the usual "Scott correction" in these units. An exact calculation of $E(h)$ shows that the term $0(h^{-1})$ in (2.15) oscillates with amplitude $\sim h^{-1}$ as $h \to 0$ (see "model (a)" in [21]). In this sense, (2.14) gives the best possible asymptotics for $E(h)$.

<u>Example</u> <u>2:</u> Let $V(x) = |x|^2$. As in example 1, the eigenvalues are known explicitly:

$$e_{\ell mns}(h) = h(2\ell+2m+2n+3); \quad \ell,m,n \in \{0,1,2,\ldots\},\ s = 1,2,\ldots,q\,.$$

Direct calculation gives

$$N_h(e) = h^{-3}N_c(e) + h^{-2}n(e,h), \qquad N_c(e) = \frac{q}{6}e^3$$

and $\Psi_h(e) = h^{-3}\,\frac{q}{24}\,e^4 + h^{-1}\,\psi(e,h)$. Again, $|n(e,h)|$, $|\psi(e,h)|$ are each bounded for $h \in (0,h_0]$, $e \in [0,e_0]$, where h_0, e_0 are any positive numbers. The theorem gives

$$E(h) = \frac{3}{4}\left(\frac{6}{q}\right)^{1/3} h^{-3} + 0(h^{-1}). \tag{2.16}$$

In this case we have no "Scott term." A direct calculation of $E(h)$ shows that (2.16) gives the best possible asymptotics for $E(h)$.

<u>Proof</u> <u>of</u> <u>Theorem</u> <u>1</u>: First define $\mu_1(h)$ so that $\mu_h = \mu_0 + h\mu_1(h)$. Using

this with (2.8), (2.9) and (2.10),

(2.17) $$E(h) = h^{-3}\mu_0 + h^{-2}\mu_1(h) - \Psi_h(\mu_0) - \int_{\mu_0}^{\mu_0+h\mu_1} N_h(e)\,de$$

$$= h^{-3}\mu_0 - \Psi_h(\mu_0)$$

$$+ h^{-3}\int_{\mu_0}^{\mu_0+h\mu_1}(1 - N_c(e))\,de - h^{-2}\int_{\mu_c}^{\mu_0+h\mu_1} n(e,h)\,de.$$

We show that these last two terms are $0(h^{-1})$ as $h \to 0$ to obtain the desired result.

To this end, we first show that $\mu_1(h)$ is bounded for h sufficiently small. From (2.6) we see that $N_c(e)$ is continuous and strictly increasing for those e such that $0 < N_c(e) < +\infty$. From our hypotheses, $1 < N_c(\mu_0 + \epsilon) < +\infty$, so we may choose $\delta \in (0,\frac{1}{2})$ sufficiently small so that $N_c^{-1}([1-\delta, 1+\delta]) \subset [\mu_0 - \frac{\epsilon}{2}, \mu_0 + \frac{\epsilon}{2}]$. Let $h_1 = \min\{h_0, \frac{\delta}{n_{max}}\}$. Recalling (2.7) and (2.9), we have

$$\mu_h = \min\{e : N_c(e) + hn(e,h) \geq 1\},$$

which gives, for $h \in (0,h_1]$,

(2.18) $$\mu_h \in N_c^{-1}([1 - hn_{max}, 1 + hn_{max}]).$$

Taking the derivative in (2.6), we find that $N_c'(e)$ exists and is finite, continuous and nondecreasing for $-\infty < e < \mu_0 + \frac{\epsilon}{2}$. Also, $N_c'(e) > 0$ when $N_c(e) > 0$. Using this with (2.18) yields

$$|\mu_h - \mu_0| \leq h\,n_{max}\,\frac{1}{N_c'(N_c^{-1}(1-\delta))}$$

or

(2.19) $$|\mu_1(h)| \leq \frac{n_{max}}{N_c'(N_c^{-1}(1-\delta))} \qquad \text{for } h \in (0,h].$$

For the last term in (2.17) we have the bound

$$\left|h^{-2}\int_{\mu_0}^{\mu_0+h\mu_1} n(e,h)\,de\right| \le h^{-1}|\mu_1(h)|\, n_{max} \tag{2.20}$$

for $h \in (0,h_1]$, and so this term is $O(h^{-1})$ as $h \to 0$. The second-to-last term in (2.17) is bounded by

$$\left|h^{-3}\int_{\mu_0}^{\mu_0+h\mu_1}(1-N_c(e))\,de\right| = \left|h^{-3}\int_0^{h\mu_1}(N_c(\mu_0)-N_c(\mu_0+e))\,de\right| \tag{2.21}$$

$$\le h^{-3}\left(\int_0^{h|\mu_1|} e\,de\right) \max_{|e|\le h|\mu_1|} N_c'(\mu_0+e)$$

$$\le h^{-1}\,|\mu_1(h)|^2\, N_c'(\mu_0+\tfrac{\epsilon}{2}) \qquad \text{for } h \in (0,h_1].$$

Equations (2.17), (2.19), (2.20) and (2.21) give the desired result (2.14) for $h \in (0,h_1]$.

CHAPTER III

Spectral Asymptotics for a Class of Potentials

This chapter is devoted to determining the asymptotic form of the functions N_h and Ψ_h as $h \to 0$ for a class of potentials, $\mathcal{V}$, to be described shortly. The functions N_h and Ψ_h were introduced in Chapter II. Our goal here is to prove that N_h satisfies the hypotheses of Theorem 1, and then to prove that Ψ_h is of such a form that E(h) has no "Scott correction" for potentials in class $\mathcal{V}$.

An outline of the arguments will be given in this chapter, leaving the details of the proofs to Appendices A and B. Also in this chapter we shall let $q \equiv$ "number of spin states of the fermions" assume the value $q = 1$. This is because q appears only as a multiplicative factor in N_h and Ψ_h. It should be noted that E(h) does not depend on q in this simple manner.

The methods used in this Chapter are those of Chazarain [4] and Helffer and Robert [7]. The new content here is in evaluating the "second term" in the small h asymptotics and the straightforward extension of their methods to Ψ_h.

First we shall define the class of potentials to be considered (see [4]). Let $\mathcal{V}$ be the set of all real valued, C^∞-functions V on $\mathbb{R}^n$ which satisfy as $|x| \to +\infty$:

$$(3.1) \qquad \begin{cases} \partial_x^\alpha V(x) = 0(|x|^{2-|\alpha|}) & \text{for } 0 \le |\alpha| \le 2 \\ \partial_x^\alpha V(x) = 0(1) & \text{for } |\alpha| \ge 2 \end{cases},$$

and

(3.2) $$V(x) \geq c|x|^2 \text{ for some } c > 0.$$

For our purpose of outlining the arguments in this chapter, (3.1) will not appear in what follows. It, along with (3.2), will be used in Appendix A to produce bounds on the phase, S, and amplitudes, a_j, in a geometric optics expansion, which will be introduced later in this chapter. The primary consequence of (3.2) to be used in this chapter is that N_h is a tempered distribution. Finally, in this chapter we will work with potentials $V(x)$ for $x \in \mathbb{R}^n$. Although we are primarily interested in the $n = 3$ dimensional case, the case of more general $n \geq 3$ is no more difficult.

For all $V \in \mathcal{V}$, $H = -h^2\Delta + V$ is self-adjoint and has a spectrum composed of eigenvalues $\{e_j(h)\}_{j=1}^{\infty}$ that obey $e_j(h) \to +\infty$ as $j \to \infty$ for each fixed $h > 0$. We may apply the Cwikel-Lieb-Rosenbljum bound (see [17], Section XIII.3) to $N_h(e)$, defined in (2.5), to obtain

(3.3) $$N_h(e) \leq c_n h^{-n} \int_{V(x)\leq e} (e - V(x))^{n/2}\, d^n x.$$

Equations (3.2) and (3.3) then show that $N_h(e) \leq c' h^{-n} e^n$. Thus, we may think of $N_h \in \mathcal{S}'$ as defined by

$$(N_h, f) = \int_{-\infty}^{\infty} N_h(e)\, f(e)\, de$$

for all $f \in \mathcal{S}$. The derivative N_h' is then in $\mathcal{S}'$ and may be written as a sum of δ-functions

(3.4) $$N_h'(e) = \sum_{j=1}^{\infty} \delta(e - e_j(h)).$$

The function N_h' is often called the density of states for the quantum Hamiltonian H. Furthermore, the Fourier transform $\widehat{N_h'}$ is in $\mathcal{S}'$. We thus see that the trace of the (quantum mechanical) propagator is a tempered distribution, because formally,

$$\hat{N_h'}(t) = \int_{-\infty}^{\infty} e^{-ite} N_h'(e)\, de = \sum_{j=1}^{\infty} e^{-ite_j(h)} \tag{3.5}$$

$$= \operatorname{tr} e^{-itH}.$$

To get at N_h', which will ultimately enable us to get information on N_h and Ψ_h, we shall consider a convolution $N_h' * \theta_h$. Since we are interested in the asymptotics as $h \to 0$, it would be nice if $\theta_h \to \delta$-function as $h \to 0$. In particular, we put

$$\theta_h(t) = \frac{1}{2\pi h} \hat{\rho}(-\tfrac{t}{h}), \tag{3.6}$$

where $\rho \in C_0^\infty(\mathbb{R})$ will be chosen later. We require $\rho(0) = 1$, which makes θ_h have unit weight; that is,

$$\int_{-\infty}^{\infty} \theta_h(t)\, dt = \rho(0) = 1. \tag{3.7}$$

For technical reasons in the proof of Proposition 5, we require, as in [7], Section 5, that ρ is even, $\hat{\rho} \geq 0$ and there is some $\delta_0 > 0$ so that

$$\hat{\rho}(\sigma) > 0 \quad \text{for} \quad \sigma \in [-\delta_0, \delta_0]. \tag{3.8}$$

(To construct such a ρ, start with $\rho_1 \in C_0^\infty(\mathbb{R})$ with ρ_1 even, $\rho_1 \geq 0$ and $\rho_1(0) > 0$, then put $\rho(t) = \frac{(\rho_1 * \rho_1)(t)}{(\rho_1 * \rho_1)(0)}$.)

Since a convolution is equal to the inverse Fourier transform of a product of Fourier transforms, we have

$$(3.9)\qquad (N_h' * \theta_h)(\lambda) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{it\lambda}\, \hat{N_h'}(t)\, \hat{\theta}_h(t)\, dt$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{it\lambda} \rho(th)\, \mathrm{tr}\, e^{-itH} dt$$

$$= \frac{1}{2\pi h}\int_{-\infty}^{\infty} \rho(t)\, e^{it\lambda/h}\, \mathrm{tr}\, e^{-itH/h}\, dt.$$

(Chazarain's [4] notation $I_\tau(h) = (2\pi h)(N_h' * \theta_h)(-\tau)$ in the notation used here.)

To make further progress, we must determine the propagator $U(t) = e^{-itH/h}$, which is the unitary group that solves the Schrödinger equation. That is, if

$$(3.10)\qquad ih\partial_t \psi(t,x) = H\psi(t,x),$$

then

$$\psi(t,x) = e^{-itH/h}\psi(0,x) = U(t)\psi(0,x).$$

To this end, consider the effect of applying the propagator to a plane wave of momentum η. Make the definition

$$(3.11)\qquad A_h(t,x,\eta)e^{iS(t,x,\eta)/h} = e^{-itH/h}\, e^{i\eta\cdot x/h}$$

Clearly, there is some freedom in choosing A_h and S, and the choice we make is that S does not depend on h. Putting (3.11) into the Schrödinger equation (3.10) gives

$$(3.12)\qquad \partial_t S + |\partial_x S|^2 + V(x) = 0, \quad S(0,x,\eta) = \eta\cdot x;$$

$$(3.13)\qquad \partial_t A_h + 2\partial_x S\cdot\partial_x A_h + (\Delta S)A_h = ih\Delta A_h, \quad A_h(0,x,\eta) = 1.$$

The first of these (3.12) is just the Hamilton-Jacobi equation from classical mechanics. The second (3.13) is usually solved by making the expansion

(3.14) $$A_h^{(N)}(t,x,\eta) = \sum_{j=0}^{N} h^j a_j(t,x;\eta),$$

where the amplitudes a_j satisfy the transport equations (which derive from (3.13)):

(3.15) $$\partial_t a_j + 2\partial_x S \cdot \partial_x a_j + (\Delta S) a_j = \begin{Bmatrix} 0 & j=0 \\ i\Delta a_{j-1} & j \geq 1 \end{Bmatrix};$$

$$a_0(0,x,\eta) = 1, \quad a_j(0,x,\eta) = 0 \text{ for } j \geq 1.$$

Formally, we expect $A_h^{(N)} \to A_h$ as $N \to \infty$ for small h. In Appendix A we will construct $A_h^{(N)}$ by solving the transport equations (3.15) for small times t and then will study how well the operator $E(t)$ defined by

(3.16) $$(E(t)f)(x) = (2\pi h)^{-n} \iint A_h^{(N)}(t,x,\eta) e^{i(S(t,x,\eta)-\eta\cdot y)/h} f(y)\,dy\,d\eta$$

approximates the operator $U(t)$. This method of constructing an approximation $E(t)$ to $U(t)$ is known as the geometric optics expansion.

Merely to outline the arguments, in this chapter we will assume we can solve (3.12) and (3.13) in some neighborhood of $t = 0$ and will write formally

(3.17) $$(U(t)f)(x) = (2\pi h)^{-n} \iint A_h(t,x,\eta) e^{i(S(t,x,\eta)-\eta\cdot y)/h} f(y)\,dy\,d\eta.$$

A way to think of (3.17) is that the integral over y decomposes f into its plane wave constituents $e^{i\eta\cdot x/h}$, and the integral over η superposes the solutions (3.11) for the time evolution of the plane waves.

Returning to our discussion of the convolution $N_h' * \theta_h$, which is a smooth approximation to N_h', we obtain from (3.9) and (3.17)

(3.18) $$(N_h' * \theta_h)(\lambda) = (2\pi h)^{-n-1} \iint_{\mathbb{R}^{2n}} \int_{-\infty}^{\infty} \rho(t) A_h(t,x,\eta) e^{i(S(t,x,\eta)-x\cdot\eta+\lambda t)/h}\,dt\,dx\,d\eta.$$

The small h asymptotics of the integral in (3.18) may be determined by the method of stationary phase. The phase function

(3.19) $$\phi(t,x,\eta,\lambda) = S(t,x,\eta) - x\cdot\eta + \lambda t$$

is stationary at the points (t,x,η), for which

(3.20a) $$\partial_t\phi = \partial_t S + \lambda = 0;$$

(3.20b) $$\partial_x\phi = \partial_x S - \eta = 0;$$

(3.20c) $$\partial_\eta\phi = \partial_\eta S - x = 0.$$

Equations (3.20a) and (3.20b) with (3.12) say that

(3.21) $$|\eta|^2 + V(x) = \lambda.$$

Equation (3.20c) implies that (t,x,η) are the period, initial position, and initial momentum, respectively, of a closed periodic classical trajectory. (This point will be made clearer in Appendix A.) Note that from (3.12) all trajectories of period zero $\{(t,x,\eta) : t = 0, (x,\eta) \in \mathbb{R}^{2n}\}$ satisfy (3.20c).

At this point we exercise our freedom in choosing $\rho \in C_0^\infty(\mathbb{R})$. Make the definitions:

$\mathcal{L}_\tau$ = set of periods of periodic classical trajectories of energy τ;

(3.22) $$\mathcal{L}_I = \bigcup_{\tau\in I} \mathcal{L}_\tau, \text{ for an interval } I \subset \mathbb{R}.$$

(Note that our $\mathcal{L}_\tau = \mathcal{L}_{-\tau}$ in [4].) In the hypotheses of the next theorem these definitions will appear, because what is desired is to take $\rho(t) = 0$ outside a small neighborhood of $t = 0$, and this neighborhood shall not include any periods, other than zero, of closed periodic classical trajectories with energy τ near λ. (That this may be done is left to Appendix A.) This condition on ρ means that in the integral (3.18) we need only concern ourselves with those points of stationary phase with $t = 0$. This set of points of stationary phase lies on the compact $(2n-1)$ - dimensional manifold

$$W_\lambda = \{(t,x,\eta) \in \mathbb{R}^{2n+1} : t = 0, |\eta|^2 + V(x) = \lambda\}. \tag{3.23}$$

Compactness of W_λ follows from (3.2).

If we further assume that λ is not a critical value of the potential V, then the phase ϕ in (3.19) will be nondegenerate over the manifold W_λ. That is, the matrix $\partial^2_{(t,x,\eta)} \phi$ will not have determinant zero anywhere on W_λ. We can now use the method of stationary phase (discussed in Appendix B) to calculate the small h asymptotic behavior of the integral (3.18). We obtain:

<u>**Theorem 2**</u>: Suppose $(\lambda_0 - \epsilon_0, \lambda_0 + \epsilon_0)$ is a bounded open interval such that V has no critical values in $[\lambda_0 - \epsilon_0, \lambda_0 + \epsilon_0]$ and that

$$\operatorname{supp} \rho \cap \bar{\mathcal{L}}_{(\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)} = \{0\}. \tag{3.24}$$

Then

$$(N'_h * \theta_h)(\lambda) = (2\pi h)^{-n} \operatorname{vol}(W_\lambda) + 0(h^{2-n}) \tag{3.25}$$

as $h \to 0$ for $\lambda \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$. Moreover, the term $0(h^{2-n})$ is uniform for $\lambda \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$. ($\theta_h$ is related to ρ in (3.6) and W_λ is given by (3.23).) The first term in (3.25) appears in [7], Theorem 3, and for one value of λ (instead of λ in an interval) in [4], Theorem 2.

Although not part of our argument here, it should be mentioned that the effect of the presence or absence of periodic closed classical trajectories of periods other than zero on N'_h or N_h has been well observed. (See [3], [4], [7],

[10], [11], and [15].) They determine the detailed structure of $N_h(e)$, that is, the oscillatory behavior of the function n(e,h) appearing in Theorem 1. Here we want only to obtain that n(e,h) is bounded as $h \to 0$, and it will not be necessary to consider the periodic closed classical trajectories of periods other than zero.

Now we move on to computing $N_h * \theta_h$ and $\Psi_h * \theta_h$. Since

$$N_h(\lambda) = \int_{-\infty}^{\lambda} N_h'(e)\, de,$$

we have

$$(N_h * \theta_h)(\lambda) = \int_{-\infty}^{\lambda} (N_h' * \theta_h)(\tau)\, d\tau. \tag{3.26}$$

Using (3.18) in (3.26) and recalling (3.19) then gives

$$(N_h * \theta_h)(\lambda) = (2\pi h)^{-n-1} \int_{-\infty}^{\lambda} \iint_{\mathbb{R}^{2n}} \int_{-\infty}^{\infty} \rho(t) A_h(t,x,\eta) e^{i\phi(t,x,\eta,\tau)/h}\, dt\, dx\, d\eta\, d\tau. \tag{3.27}$$

Apply the method of stationary phase (modulo a technical point to be mentioned shortly) to the integration over (t,τ) in (3.27). The phase is stationary for

(3.28a) $\quad \partial_t \phi \;=\; \partial_t S + \tau = 0;$

(3.29b) $\quad \partial_\tau \phi \;=\; t = 0.$

Equations (3.28a and b) combined with (3.12) give

$$\{(t,\tau) : t = 0,\ \tau = |\eta|^2 + V(x)\} \tag{3.29}$$

as the stationary point of the phase ϕ. The method of stationary phase then yields:

<u>**Theorem 3**</u>: Under the same hypotheses as Theorem 2,

$$(N_h * \theta_h)(\lambda) = (2\pi h)^{-n} \iint_{|\eta|^2 + V(x) \le \lambda} dx\, d\eta + O(h^{1-n}) \tag{3.30}$$

as $h \to 0$ for $\lambda \in (\lambda_0 - \epsilon_0, \lambda_0 + \epsilon_0)$. Moreover, the term $O(h^{1-n})$ is uniform in λ. (The result (3.30) appears in [7], Proposition 5.1, for a single value of λ.)

For $\Psi_h * \theta_h$, note that from (2.5) and (3.26),

$$(3.31) \qquad (\Psi_h * \theta_h)(\lambda) = \int_{-\infty}^{\lambda} (\lambda - \tau)(N_h' * \theta_h)(\tau)\, d\tau,$$

which gives, using (3.18),

$$(3.32) \qquad (\Psi_h * \theta_h)(\lambda) = (2\pi h)^{-n-1} \int_{-\infty}^{\lambda} \iint_{\mathbb{R}^{2n}} \int_{-\infty}^{\infty} (\lambda - \tau)\rho(t) \cdot A_h(t,x,\eta) e^{i\phi(t,x,\eta,\tau)/h}\, dt\, dx\, d\eta\, d\tau.$$

Applying the method of stationary phase as in the case of $N_h * \theta_h$, but calculating to higher order in h, yields:

<u>Theorem 4</u>: Under the same hypotheses as Theorem 2, for $\lambda \in (\lambda_0 - \epsilon_0, \lambda_0 + \epsilon_0)$,

$$(3.33) \quad (\Psi_h * \theta_h)(\lambda) = (2\pi h)^{-n} \iint_{|\eta|^2 + V(x) \leq \lambda} (\lambda - |\eta|^2 - V(x))\, dx\, d\eta + O(h^{2-n})$$

as $h \to 0$.

Several technical points that will be dealt with in Appendix A should be pointed out. As has already been indicated, we will be using $A_h^{(N)}$ in (3.14) in place of A_h in the integrals (3.18), (3.27) and (3.32). This error will be shown to contribute at an order of h higher than we are interested in for N sufficiently large. Also, the convergence of these three integrals needs attention.

In the integrals (3.27) and (3.32) there is a "sharp edge" on the (t,τ) region of integration at $\tau = \lambda$. The method of stationary phase that is discussed in

Appendix B cannot be applied in such situations because everything must be smooth. We will also have to consider the region of negative τ separately. To remedy this, we take three smooth functions to make these cuts. For $\lambda \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$ fixed, choose $\chi_1, \chi_2, \chi_3 \in C^\infty(\mathbb{R})$ so that

$$\begin{aligned} &\operatorname{supp} \chi_1 \subset (-\infty, -1] \\ &\operatorname{supp} \chi_2 \subset [-2, \lambda-\tfrac{\epsilon}{2}] \\ &\operatorname{supp} \chi_3 \subset [\lambda-\epsilon, +\infty) \\ &\chi_1(\tau)+\chi_2(\tau)+\chi_3(\tau) \equiv 1 \quad \text{for} \quad \tau \in \mathbb{R}, \end{aligned} \tag{3.34}$$

where $\epsilon > 0$ is sufficiently small so that $\lambda-\epsilon > \lambda_0-\epsilon_0$, where $(\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$ is as in Theorem 2. We put (3.34) in the integrands of (3.27) and (3.32). The χ_1 terms will be treated separately in Appendix A and will contribute $0(h^{+\infty})$ as $h \to 0$. The χ_2 terms are treated using the method of stationary phase (now the integrands are smooth) as we have just described. The χ_3 terms will be computed by integrating the result of Theorem 2 for $\tau \in [\lambda-\epsilon, \lambda]$. In the sum of these terms, the χ-functions will drop out and we obtain Theorems 3 and 4. This is the reason we need Theorem 2, which is shown by a different application of the method of stationary phase than is used in Theorems 3 and 4.

At this point we need to recover the small h asymptotic form of N_h and Ψ_h, which are of primary interest to us, from the small h asymptotic forms of $N_h * \theta_h$ and $\Psi_h * \theta_h$, which we were able to compute. The following result makes this connection.

<u>Proposition 5</u>: Under the hypotheses of Theorem 2, we have

$$N_h(\lambda) - (N_h * \theta_h)(\lambda) = 0(h^{1-n}) \tag{3.35}$$

as $h \to 0$, uniformly for $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$. Also,

(3.36) $$\Psi_h(\lambda) - (\Psi_h * \theta_h)(\lambda) = 0(h^{2-n}) \text{ for } \lambda \in (\lambda_0 - \tfrac{\epsilon_0}{2}, \lambda_0 + \tfrac{\epsilon_0}{2}).$$

Combining Theorems 3 and 4 with Proposition 5 gives the desired result of this chapter:

<u>Theorem</u> <u>6</u>: Suppose $V \in \mathcal{V}$ and that λ_0 is not critical for V. Let $\epsilon_0 > 0$ so that V has no critical values in $[\lambda_0 - \epsilon_0, \lambda_0 + \epsilon_0]$. Then

(3.37) $$N_h(\lambda) = (2\pi h)^{-n} \iint_{|\eta|^2+V(x)\leq\lambda} dx\, d\eta + 0(h^{1-n})$$

as $h \to 0$ and $0(h^{1-n})$ is uniform for $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$. Also, for $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$,

(3.38) $$\Psi_h(\lambda) = (2\pi h)^{-n} \iint_{|\eta|^2+V(x)\leq\lambda} (\lambda - |\eta|^2 - V(x))\, dx\, d\eta + 0(h^{2-n}).$$

In Chapter IV we conclude that if the semiclassical Fermi level, μ_0, defined in (2.11), is not critical for $V \in \mathcal{V}$, then E(h) in (2.2) has no "Scott correction."

CHAPTER IV

Conclusions

In this final chapter we present our main result as Theorem 7. We then discuss extending this result to a larger class of potentials and the difficulty encountered if the potential is singular.

Theorem 7: Let the number of dimensions $n = 3$, $V \in \mathcal{V}$ and μ_0 be as in (2.11). If μ_0 is not a critical value of V, then for E(h) in (2.2)

$$E(h) = c_1 h^{-3} + 0(h^{-1}) \quad \text{as } h \to 0, \tag{4.1}$$

where the constant c_1 is as predicted by the Thomas-Fermi model. In terms of $Z = h^{-3}$, this says that the ground state energy of the Hamiltonian H(Z) in (2.1) is given by

$$E(Z) = c_1 Z^{7/3} + 0(Z^{5/3}) \quad \text{as } Z \to +\infty, \tag{4.2}$$

and so there is no "Scott term."

Proof: This is an immediate corollary to Theorems 1 and 6 with

$$c_1 = \mu_0 - (2\pi)^{-3} q \iint_{|\eta|^2 + V(x) \leq \mu_0} (\mu_0 - |\eta|^2 - V(x))\, d^3x\, d^3\eta . \tag{4.3}$$

That c_1 is as in the Thomas-Fermi theory is all that needs comment. The Thomas-Fermi energy functional for the Hamiltonian (2.1) is (after the changes of variables made in Chapter II)

$$\mathcal{E}(\rho;h) = h^{-3}\left\{\tfrac{3}{5}\gamma \int \rho^{5/3}(x)\, d^3x + \int \rho(x)\, V(x) d^3x\right\}, \tag{4.4}$$

where $h^{-3}\rho(x)$ is the particle density that must satisfy

$$\int \rho(x)\, d^3x = 1 \tag{4.5}$$

and $\gamma = \left(\frac{6\pi^2}{q}\right)^{2/3}$. Minimizing (4.4) with the constraint (4.5) gives

$$\rho(x) = \frac{q}{6\pi^2} (\lambda - V(x))_+^{3/2}, \tag{4.6}$$

where λ is a Lagrange multiplier. From (4.5) we must have $\lambda = \mu_0$. Using (4.6) in (4.4) then gives

$$\mathcal{E}(\rho;h) = h^{-3} \left\{\mu_0 - \frac{q}{15\pi^2} \int_{V(x)\leq\mu_0} (\mu_0 - V(x))^{5/2}\, d^3x\right\}. \tag{4.7}$$

Thus, (4.7) and (4.1) agree to leading order if we do the integral over η in (4.3). This completes the proof of Theorem 7.

A few words are in order on the physical meaning of the hypothesis that the semiclassical Fermi level, μ_0, is not critical for V. If μ_0 were critical for V, then the phase ϕ in (3.19) would be degenerate at some points on the manifold W_{μ_0} in (3.23). In the evaluation by the method of stationary phase of $N'_h * \theta_h$, the successive asymptotic terms would decrease by h^δ for some $\delta < 1$. This would carry over to N_h and Ψ_h and would finally give $E(h) = c_{TF} h^{-3} + 0(h^{-3+2\delta})$. This last term means that E(h) may oscillate more widely about $c_{TF} h^{-3}$ than if μ_0 were not critical for V.

It should be possible to extend the results of Chapter III, and hence Theorem 7, to potentials that do not grow at infinity, by using the functional calculus developed by Helffer and Robert [8]. They extend Theorem 3 to a broad class of smooth potentials, which includes, for example

$$V(x) = -(1 + |x|^2)^d, \quad d < 0.$$

They are able to do this by using their functional calculus to smoothly truncate the operator H below the continuous spectrum and then by proceeding similarly to Chapter III.

For potentials that have singularities, for example,

$$V(x) = -|x|^{-a}, \qquad 0 < a < 2, \tag{4.8}$$

one has the immediate difficulty that V is no longer smooth or bounded. The assumption that V is smooth and bounded is often used in Appendix A in the proofs of the results of Chapter III. Worse still, formal calculations of N_h and Ψ_h in terms of V, such as those in [1], give asymptotic series that decrease in powers of h^2. That is, we might compute something like

$$(4.9) \qquad \begin{aligned} N_h(\lambda) &= h^{-3}A(\lambda) + h^{-1}B(\lambda) + \cdots \\ \Psi_h(\lambda) &= h^{-3}C(\lambda) + h^{-1}D(\lambda) + \cdots. \end{aligned}$$

Thus, if V is such that for some $\delta > 0$,

$$(4.10) \qquad E(h) = c_{TF}\, h^{-3} + c_2 h^{-1+\delta} + \cdots,$$

then $D(\mu_0)$ in (4.9) is found to be infinite. This is not surprising, but knowing $D(\mu_0)$ is infinite does not then tell us what δ should be in (4.10). Here lies the main difficulty in finding, even from a formal calculation, the first correction to E(h) if it is less that two orders in h down from the leading term, which may be the case for a singular potential (e.g., $V(x) = -|x|^{-1}$ in Example 1 of Chapter II).

We now present a very rough calculation that perhaps sheds some light on the origin of the Scott correction in the case of singular potentials. Let V be of the form given in (4.8). Then the eigenvalues $e_j(h)$ of $H = -h^2\Delta + V$ are given very approximately by inverting

$$h^{-3}N_C(e_j(h)) \doteq j, \qquad j = 1,2,3,\ldots,$$

which gives, using (4.8) and (2.6)

$$(4.11) \qquad e_j(h) \sim -h^{-3b} j^{-b},$$

where $b = \frac{2a}{3(2-a)}$. We then have

$$(4.12)\qquad E(h) = \sum_{j=1}^{h^{-3}} e_j(h) \sim -h^{-3b} \sum_{j=1}^{h^{-3}} j^{-b}$$

$$= \begin{cases} -\frac{1}{1-b} h^{-3} - \gamma(b) h^{-3b} + 0(1), & 0 < a < \frac{6}{5} \text{ or } b < 1, \\ -h^{-3}(\log h^{-3} + \gamma) + 0(1), & a = \frac{6}{5} \text{ or } b = 1 \\ -\zeta(b) h^{-3b} + \frac{1}{b-1} h^{-3} + 0(1), & \frac{6}{5} < a < 2 \text{ or } b > 1 \end{cases}$$

where ζ is the zeta function, $\gamma \doteq .5772$ is Euler's constant, and

$$\gamma(\beta) = \lim_{m \to \infty} \Big(\sum_{n=1}^{m} n^{-\beta} - \int_0^m n^{-\beta}\, dn \Big).$$

Note that for $a = 1$ (Coulomb potential) we have, from (4.12),

$$E(h) \sim (-3h^{-3} + 2.45 h^{-2} + \cdots),$$

which is of the right form, although the ratio of the coefficients is not quite right.

The point in computing (4.12) is to point out that what we would naturally call the "Scott corrections" are the h^{-3b} terms. This suggests that the Scott correction for potentials of the form (4.8) is of the same order in h as that of the energies in (4.11). If $V(x)$ were of the form (4.8) only for $|x|$ near zero, then we would still expect the Scott correction to occur at order h^{-3b}, because the lowest states would still scale as in (4.11), and they would be the dominant terms in the sum (4.12). This is just an extension of Scott's intuition to the more general singularity considered here. If this idea is true, namely, that the Scott correction depends on h (or Z) in the same manner as the ground state in a singular potential, then it is an accident of the particular form of the atomic potential singularity (it is Coulomb) that one obtains in (1.3) what looks like an asymptotic series in h or $Z^{-1/3}$. That is, the Scott correction might occur at a different order than Z^2 if the nuclear potential singularity were other than Coulomb.

Finally, we mention that it may be possible to find a way to combine the methods of Siedentop and Weikard [22] with the methods of this thesis to produce an upper bound for the multinucleus or molecular Scott correction problem. It is tempting to try to cut the problem into two parts, treat the nearly spherically symmetric nuclear Coulomb singularities with the ideas in [22], and then treat the electrons in the unsymmetric but smooth potential away from the nuclei using the ideas in this thesis. But it is not at all clear how to make this "cut."

APPENDIX A

Mathematical Detail

The purpose of this appendix is to review the results of Chazarain [4] and Helffer-Robert [7], and to extend their methods to compute the leading small h asymptotic form of Ψ_h to two orders. A discussion of the method of stationary phase follows in Appendix B.

<u>Some preliminaries</u>

Let

$$\mathfrak{D} = \{\psi \in L^2 : \Delta\psi \in L^2 \text{ and } |x|^2\psi \in L^2\}.$$

For any potential $V \in \mathcal{V}$, the operator

$$H = -h^2\Delta + V$$

is self-adjoint on $\mathfrak{D}$, positive, and is an isomorphism from $\mathfrak{D}$ to L^2. The spectrum of H consists of a discrete set of positive eigenvalues of finite multiplicity $\{e_j(h)\}$. Let $\{\phi_j\}$ be the corresponding set of orthonormal eigenfunctions of H; then $\phi_j \in \mathcal{S}(\mathbb{R}^n)$ all j. (For these results, see [2], Section 7. Use $\varphi(x,\xi) \equiv 1$, $\Phi(x,\xi) = (1+|x|^2+|\xi|^2)^{1/2}$ as weight functions.)

The unitary group generated by H is $U(t) = e^{-itH/h}$ and is a bounded operator on L^2. The unitary group solves the Schrödinger equation (3.10), and we may write the explicit formula

$$(U(t)\psi)(x) = \sum_{j=1}^{\infty} e^{-ite_j(h)/h}\phi_j(x) \int \overline{\phi_j(y)}\, \psi(y)\, dy$$

for $\psi \in L^2$. The distribution $\mathrm{tr}\, e^{-itH/h} = \mathrm{tr}\, U(t)$ is defined as follows for $\theta \in \mathcal{S}(\mathbb{R})$:

$$\langle \mathrm{tr}\ U(t), \theta(t)\rangle = \mathrm{tr}\ U_\theta,$$

where

$$U_\theta = \int_{-\infty}^{\infty} \theta(t)\ U(t)\ dt.$$

To see that the trace is finite, note that

$$\begin{aligned}(U_\theta \psi)(x) &= \int_{-\infty}^{\infty} \theta(t) \sum_{j=1}^{\infty} e^{-ite_j(h)/h}\ \phi_j(x) \int \overline{\phi_j(y)}\psi(y)\,dy\,dt \\ &= \int \Big[\sum_{j=1}^{\infty} \hat\theta(\tfrac{e_j}{h})\ \phi_j(x)\ \overline{\phi_j(y)} \Big]\ \psi(y)\ dy,\end{aligned}$$

because the sums converge absolutely. Thus,

$$\mathrm{tr}\ U_\theta = \sum_{j=1}^{\infty} \hat\theta(\tfrac{e_j}{h})$$

is finite since $\hat\theta \in \mathcal{S}$. Moreover,

$$\begin{aligned}\text{(A.1)} \qquad \langle \mathrm{tr}\ U(t), \theta(t)\rangle &= \langle N_h'(e), \hat\theta(\tfrac{e}{h})\rangle \\ &= \langle \hat{N_h'}(\tfrac{t}{h}), \theta(t)\rangle,\end{aligned}$$

from which we see that $\hat{N_h'}(\frac{t}{h}) = \mathrm{tr}\ e^{-itH/h}$, which we used in (3.9).

<u>Solutions to the Hamilton-Jacobi equation and the transport equations</u>

We will later need an estimate for $\partial_t S$, where S is the solution of the Hamilton-Jacobi equation (3.12). From the general theory of first-order partial differential equations, we can solve (3.12) for S, once we know the solutions $(x(t,y,\eta), \xi(t,y,\eta))$ of the characteristic equations (which are just Hamilton's equations of motion):

$$\text{(A.2)} \qquad \begin{aligned}\partial_t x &= \partial_\xi(|\xi|^2 + V(x)) &&= 2\xi, && x(0,y,\eta) = y; \\ \partial_t \xi &= -\partial_x(|\xi|^2 + V(x)) &&= -\partial_x V(x), && \xi(0,y,\eta) = \eta.\end{aligned}$$

Since the energy is constant

$$\text{(A.3)} \qquad |\xi|^2 + V(x) = |\eta|^2 + V(y)$$

and $V(x) \to +\infty$ as $|x| \to +\infty$, the solution (x,ξ) of (A.2) exists and remains bounded for all $t \in \mathbb{R}$.

From the equations (A.2), and making use of the hypotheses on V in (3.1) and (3.2), it is shown in [4], Section IV, that (3.12) has a C^∞ solution $S(t,x,\eta)$, $(t,x,\eta) \in [-T,T] \times \mathbb{R}^{2n}$ for some $T > 0$, and we have

$$\text{(A.4)} \qquad \begin{aligned} \partial_x S(t,x,\eta) &= \xi(t,x,\eta); \\ \partial_\eta S(t,x,\eta) &= y(t,x,\eta). \end{aligned}$$

It is shown that

$$\text{(A.5)} \qquad \left|\partial_t S(t,x,\eta)\right| \geq C\,\lambda^2(x,\eta)$$

for $C > o$ independent of $|t| \leq T$ and where $\lambda(x,\eta) = (1+|x|^2+|\eta|^2)^{1/2}$. Also, one has

$$\text{(A.6)} \qquad \partial_t^p\, \partial_\eta^\alpha\, \partial_x^\beta\, S(t,x,\eta) = 0(\lambda^p(x,\eta))$$

for $p + |\alpha| + |\beta| \geq 1$.

The transport equations (3.15) are solved for $|t| \leq T$ in [4], Section V, by a clever change of variables and by integrating along the characteristics given by (A.2). It is then shown that

$$\text{(A.7)} \qquad \partial_t^p\, \partial_\eta^\alpha\, \partial_x^\beta\, a_j(t,x,\eta) = 0(\lambda^p(x,\eta))$$

for $p + |\alpha| + |\beta| \geq 0$ and $|t| \leq T$.

Error made in using E(t) in place of U(t)

For some integer N, which may be chosen at our convenience, define $E(t)$ for $|t| \leq T$ by the expression (3.16) for all $f \in \mathcal{S}(\mathbb{R}^n)$. Let $F(t) = E(t) - U(t)$. As discussed in [4], Section VI,

$$\sup_{|t|\leq T} \|E(t)\|_{\mathcal{L}(L^2,L^2)} = 0(1);$$

$$\sup_{|t|\leq T} \|F(t)\|_{\mathcal{L}(L^2,L^2)} = 0(h^{N+2-n}),$$

and so $E(t)$ and $F(t)$ may be extended to bounded operators over all of $L^2(\mathbb{R}^n)$.

For $\theta \in C_0^\infty((-T,T))$, define the bounded operator

$$E_\theta = \int_{-T}^{T} \theta(t)\, E(t)\, dt.$$

The kernel of E_θ is then in $\mathcal{S}(\mathbb{R}^n \times \mathbb{R}^n)$ ([4], Proposition 7.1), and we may then define tr $E(t)$ as a distribution over $C_0^\infty((-T,T))$ by

$$\langle \operatorname{tr} E(t), \theta(t) \rangle = \operatorname{tr} E_\theta .$$

Define F_θ and tr $F(t)$ in a similar manner. One then has

Proposition: ([4], Proposition 9.1) For all integers M, one may choose the integer N in (3.14) so that there is a constant C such that

$$\text{(A.8)} \qquad |\langle \operatorname{tr} F(t), \theta(t)\rangle| \leq C\, h^M \sup_{0 \leq j \leq 2n} \left|\theta^{(j)}(t)\right|$$

for all $\theta \in C_0^\infty((-T,T))$.

This proposition tells us the error made in replacing $U(t)$ by $E(t)$ in the calculation of $N_h' * \theta_h$, $N_h * \theta_h$ and $\Psi_h * \theta_h$.

Proof of Theorem 2: From (3.9) and (A.1)

$$(N_h' * \theta_h)(\lambda) = \frac{1}{2\pi h} \langle \operatorname{tr} U(t), \rho(t)\, e^{it\lambda/h} \rangle$$

and so, from (A.8),

$$\text{(A.9)} \qquad \left|(N_h' * \theta_h)(\lambda) - \frac{1}{2\pi h} \langle \operatorname{tr} E(t), \rho(t)\, e^{it\lambda/h} \rangle\right|$$

$$\leq C h^{M-1} \sup_{0 \leq j \leq 2n} \left|\partial_t^j\, (\rho(t) e^{-it\lambda/h})\right|.$$

The sup above is bounded since ρ is fixed and λ is in a bounded interval. By choosing N large enough in (3.16), we may then use $E(t)$ in place of $U(t)$ in our calculation of $N_h' * \theta_h$, because the error committed in this replacement is at a higher order in h than we are interested in.

Now

$$\text{(A.10)}\qquad \begin{aligned} &\frac{1}{2\pi h}\langle \operatorname{tr}\, E(t),\ \rho(t)\, e^{it\lambda/h}\rangle \\ &= (2\pi h)^{-n-1} \iiint \rho(t)\, A^{(N)}(t,x,\eta)\, e^{i(S(t,x,\eta)-x\cdot\eta+\lambda t)/h}\, dt\, dx\, d\eta \end{aligned}$$

which, as just noted, is a good approximation to (3.18). The phase in this integral is stationary at those points (t,x,η) satisfying (3.20). From (A.2) and (A.4), the graph of the classical Hamiltonian flow for $|t| \leq T$ is

$$\{(x,\partial_x S(t,x,\eta);\ \ \partial_\eta S(t,x,\eta),\eta) : (x,\eta) \in \mathbb{R}^{2n}\}.$$

So (3.20b and c) tell us that t must be a period of a periodic classical trajectory. The condition (3.24) tells us that the only such period we need to be concerned with in evaluating (A.10) is $t = 0$. The point (x,η) must also be on the λ energy surface (3.21), and so we have a manifold of points of stationary phase W_λ given in (3.23).

At a given point $(0,x,\eta) \in W_\lambda$, we have, for the phase (3.19)

$$\phi'' = \begin{bmatrix} 2\eta\cdot\partial_x V & -\partial_x V & -2\eta \\ -\partial_x V & 0 & 0 \\ -2\eta & 0 & 0 \end{bmatrix}.$$

The subspace perpendicular to W_λ at $(0,x,\eta)$ is

$$\operatorname{span}\{(1,0,0),\ (0,\partial_x V,\ 2\eta)\}.$$

On this subspace ϕ'' is the 2×2 matrix

$$\phi''_{\perp} = \begin{bmatrix} 2\eta\cdot\partial_x V & -|\partial_x V|^2-4|\eta|^2 \\ -|\partial_x V|^2-4|\eta|^2 & 0 \end{bmatrix}$$

and

$$\det \phi''_{\perp} = -(|\partial_x V|^2 + 4|\eta|^2)^2 .$$

This may be zero only if $\eta = 0$ and $\partial_x V = 0$, and so, by (3.21), λ would have to be critical for V. Thus, $\phi''_{\perp}$ is nondegenerate for all $(t,x,\eta) \in W_\lambda$ and $\lambda \in [\lambda_0-\epsilon_0,\lambda_0+\epsilon_0]$. Also, both $|\det \phi''_{\perp}|^{-1/2}$ and $\|\phi''_{\perp}{}^{-1}\|$ are bounded uniformly for $(t,x,\eta) \in W_\lambda$ and $\lambda \in [\lambda_0-\epsilon_0,\lambda_0+\epsilon_0]$.

To evaluate (A.10), it is convenient to work in new coordinates $(t,\tau,\omega) \in \mathbb{R}\times\mathbb{R}\times\mathbb{R}^{2n-1}$, where t is the same as before, $\tau = |\eta|^2 + V(x)$ and ω denotes the remaining $(2n-1)$ coordinates. (It may be necessary to make a partition of unity over $\bigcup_{\lambda\in[\lambda_0-\epsilon_0,\lambda_0+\epsilon_0]} W_\lambda$ and choose the coordinates ω in each partition, in which case we proceed in each partition as in the following, and then sum over the partition.) In these coordinates, $W_\lambda = \{(t,\tau,\omega) : t = 0, \tau = \lambda, \text{ all } \omega\}$, and on W_λ

$$\phi''_{\perp} = \begin{bmatrix} \partial_{tt}S & -1 \\ -1 & 0 \end{bmatrix}.$$

The integral (A.10) may then be evaluated using the results of Appendix B

$$(2\pi h)^{-n-1}\iiint \rho(t)\, A^{(N)}(t,\tau,\omega)\, e^{\,i\phi(t,\tau,\omega,\lambda)}\left|\frac{\partial(x,\eta)}{\partial(\tau,\omega)}\right| dt\, d\tau\, d\omega$$

$$= (2\pi h)^{-n}\int\left\{\rho(0)\, A^{(N)}(0,\lambda,\omega)\left|\frac{\partial(x,\eta)}{\partial(\tau,\omega)}\right|_{\tau=\lambda}\right\} d\omega + O(h^{2-n}),$$

where the term $O(h^{2-n})$ is uniform for $\lambda \in (\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)$. To see that the $O(h^{1-n})$ contribution is zero, apply the result from Appendix B and use (3.7), (3.15) and note that the resulting integrand is odd in η. Finally, for the leading term, we have

$$\int \left|\frac{\partial(x,\eta)}{\partial(\tau,\omega)}\right|_{\tau=\lambda} d\omega = \mathrm{vol}(W_\lambda).$$

This completes the proof of Theorem 2.

Proof of Theorem 3: We start with (3.26) and use our partition of unity satisfying (3.34). Thus,

$$\text{(A.11)}\quad (N_h*\theta_h)(\lambda) = \int_{-\infty}^{-1} \chi_1(\tau)(N_h'*\theta_h)(\tau)\, d\tau$$
$$+ \int_{-\infty}^{\lambda-\epsilon/2} \chi_2(\tau)\, (N_h'*\theta_h)(\tau)\, d\tau$$
$$+ \int_{\lambda-\epsilon}^{\lambda} \chi_3(\tau)\, (N_h'*\theta_h)(\tau)\, d\tau .$$

We now show that the first integral is $0(h^{+\infty})$, evaluate the second by the method of stationary phase, and use Theorem 2 to evaluate the third integral.

Concerning the first integral in (A.11), we note

$$(N_h'*\theta_h)(\tau) = \frac{1}{2\pi h} \sum_{j=1}^{\infty} \hat{\rho}\left(\frac{e_j(h)-\tau}{h}\right),$$

where we have used (3.4) and (3.6). Since $\hat{\rho} \in \mathcal{S}(\mathbb{R}^n)$, for each integer $M \geq 0$ there is a constant C_M such that

$$\left|\hat{\rho}\left(\frac{e_j(h)-\tau}{h}\right)\right| \leq C_M h^M \left|e_j(h) - \tau\right|^{-M}$$

for $\tau \in (-\infty,-1]$. From (3.3) we have

$$e_j(h)^{-n} \leq C' h^{-n} j^{-1},$$

and so

$$|e_j(h)-\tau|^{-M} \le |-\tau|^{-M/2}\,|e_j(h)+1|^{-M/2}$$
$$\le (C')^{M/2n}\; h^{-M/2}|\tau|^{-M/2}\; j^{-M/2n}.$$

Thus, for each integer $M \ge 2n+1$ there is a constant C'_M such that

$$|(N'_h * \theta_h)(\tau)| \le \frac{1}{2\pi h}\, C'_M h^{M/2}\Big(\sum_{j=1}^{\infty} j^{-M/2n}\Big)\,|\tau|^{-M/2}.$$

We finally conclude that, for each integer $M \ge 2n+1$, there is a C''_M such that

$$\left|\int_{-\infty}^{-1} \chi_1(\tau)(N'_h * \theta_h)(\tau)\,dt\right| \le C''_M\, h^{M/2-1}$$

and so see that the first term in (A.11) is $O(h^{+\infty})$. Note at this point, for use in the proof of Theorem 4, that the same argument gives

$$\text{(A.12)}\qquad \left|\int_{-\infty}^{-1} \chi_1(\tau)(\lambda-\tau)(N'_h * \theta_h)(\tau)\,dt\right| \le C'''_M\, h^{M/2-1}.$$

For the second integral of (A.11), we use (A.9), and up to negligibly high order in h, we write

$$(2\pi h)^{-n-1}\iiiint \chi_2(\tau)\rho(t)N'_h(t,x,\eta)\,e^{i(S(t,x,\eta)-x\cdot\eta+\tau t)/h}\,dt\,d\tau\,dx\,d\eta.$$

First we show that the integration over distant regions of (x,η) contributes $O(h^{+\infty})$. By (A.5) there is an $R > 0$ so that

$$|\partial_t S+\tau| \ge \tfrac{1}{2} \qquad \text{for } \lambda(x,\eta) \ge R \text{ and } \tau \in [-2,\lambda-\tfrac{\epsilon}{2}].$$

Choose some $\kappa_1, \kappa_2 \in C^\infty(\mathbb{R})$ so that

$$\text{supp}\,\kappa_1 \subset [R,+\infty)$$
$$\text{supp}\,\kappa_2 \subset (-\infty,2R]$$
$$\kappa_1+\kappa_2 \equiv 1.$$

Since $-ih(\partial_t S+\tau)^{-1}\partial_t e^{i\phi_\tau/h} = e^{i\phi_\tau/h}$, repeated integrations by parts gives

(A.13) $(2\pi h)^{-n-1}\iiiint \chi_2(\tau)\rho(t)A_h^{(N)}(t,x,\eta)\kappa_1(\lambda(x,\eta))e^{i\phi(t,x,\eta,\tau)/h}dt\,d\tau\,dx\,d\eta$

$$= (2\pi h)^{-n-1}(ih)^k\iiiint\{[\partial_t(\partial_t S+\tau)^{-1}]^k \rho(t)A_h^{(N)}(t,x,\eta)\}$$

$$\cdot\ \chi_2(\tau)\kappa_1(\lambda(x,\eta))e^{i\phi(t,x,\eta,\tau)/h}dt\,d\tau\,dx\,d\eta .$$

The term in $\{\cdots\}$ times $\kappa_1(\lambda(x,\eta))$ is bounded via (A.6) and (A.7) (the integration over t then gives a convergent integral in (x,η) as in the argument showing that E_θ has kernel in $\mathcal{S}(\mathbb{R}^n\times\mathbb{R}^n)$), and so (A.13) is $O(h^{k-n-1})$ for any integer $k \geq 0$.

Thus, we need only compute

(A.14) $(2\pi h)^{-n-1}\iiiint \chi_2(\tau)\rho(t)A_h^{(N)}(t,x,\eta)\kappa_2(\lambda(x,\eta))e^{i\phi(t,x,\eta,\tau)/h}dt\,d\tau\,dx\,d\eta.$

The phase ϕ is stationary in (t,τ) at the point (3.29), at which

$$\partial^2_{(t,\tau)}\phi = \begin{bmatrix} 2\eta\cdot\partial_x V & 1 \\ 1 & 0 \end{bmatrix}.$$

Thus, $\left|\det \partial^2_{(t,\tau)}\phi\right|^{-1/2} \equiv 1$ and $\left\|\partial^2_{(t,\tau)}\phi^{-1}\right\|$ is bounded uniformly over the (x,η) region of integration. Evaluating (A.14) by the method of stationary phase then gives the result

(A.15) $$(2\pi h)^{-n}\iint \chi_2(|\eta|^2+V(x))\,dx\,d\eta + O(h^{1-n}).$$

Using Theorem 2 for the third term in (A.11) gives the result

(A.16) $(2\pi h)^{-n}\int_{\lambda-\epsilon}^{\lambda}\chi_3(\tau)\,\mathrm{vol}(W_\tau)d\tau + O(h^{2-n})$

$$= (2\pi h)^{-n}\iint_{|\eta|^2+V(x)\leq\lambda}\chi_3(|\eta|^2+V(x))\,dx\,d\eta + O(h^{2-n}).$$

Combining (A.15) and (A.16) proves Theorem 3.

Proof of Theorem 4: Start with (3.31) and proceed similarly to the proof of Theorem 3, except that we evaluate to the first two orders in h.

$$(\Psi_h * \theta_h)(\lambda) = \int_{-\infty}^{-1} \chi_1(\tau)(\lambda-\tau)(N_h' * \theta_h)(\tau)\, d\tau$$

$$+ \int_{-2}^{\lambda-\eta/2} \chi_2(\tau)(\lambda-\tau)(N_h' * \theta_h)(\tau)\, d\tau$$

$$+ \int_{\lambda-\epsilon}^{\lambda} \chi_3(\tau)(\lambda-\tau)(N_h' * \theta_h)(\tau)\, d\tau .$$

The first term on the right side above is $0(h^{+\infty})$. The second term is

(A.17) $$(2\pi h)^{-n} \iint \left\{\chi_2(|\eta|^2+V(x))\,(\lambda-|\eta|^2-V(x))\right\}\Big|_{\tau=|\eta|^2+V(x)} dx\, d\eta$$

$$+ 0(h^{2-n}).$$

The $0(h^{1-n})$ term is zero as in the proof of Theorem 2.

Using Theorem 2 on the third term gives the result

(A.18) $$(2\pi h)^{-n} \int_{\lambda-\epsilon}^{\lambda} \chi_3(\tau)\,(\lambda-\tau)\,\mathrm{vol}(W_\tau) d\tau + 0(h^{2-n})$$

$$= (2\pi h)^{-n} \iint_{|\eta|^2+V(x)\le\lambda} \chi_3(|\eta|^2+V(x))(\lambda-|\eta|^2-V(x))\, dx\, d\eta + 0(h^{2-n}).$$

Add (A.17) and (A.18) to complete the proof of Theorem 4.

Proof of Proposition 5: We shall show

Lemma 5.1: Under the hypothesis of Theorem 2, there exists a constant $C_0 > 0$ such that

(A.19) $$|N_h(\lambda+\tau h) - N_h(\lambda)| \le C_0 h^{1-n}(1+|\tau|)^{n+1}$$

for $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$, $h \in (0,1]$ and $\tau \in \mathbb{R}$.

Given this result, consider for $\lambda \in [\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2}]$,

$$(N_h * \theta_h)(\lambda) - N_h(\lambda) = \int_{-\infty}^{\infty} (N_h(\sigma) - N_h(\lambda))\theta_h(\lambda - \sigma)\, d\sigma .$$

Make the change of variable $\sigma = \lambda + \tau h$ and use (A.19) to get

$$\text{(A.20)} \qquad |(N_h * \theta_h)(\lambda) - N_h(\lambda)| \le C_0 h^{1-n} \int_{-\infty}^{\infty} (1+|\tau|)^{n+1} \theta_h(-\tau h) h\, d\tau$$

$$= C_0 h^{1-n} \frac{1}{2\pi} \int_{-\infty}^{\infty} (1+|\tau|)^{n+1} \hat{\rho}(\tau)\, d\tau,$$

where we have used (3.6) and $\hat{\rho} \ge 0$. Since $\hat{\rho} \in \mathcal{S}(\mathbb{R})$, equation (A.20) gives (3.35).

From the definition of Ψ_h in (2.8), we have

$$\Psi_h(\lambda + \tau h) - \Psi_h(\lambda) = \tau h N_h(\lambda) + \int_{\lambda}^{\lambda+\tau h} (N_h(\mu) - N_h(\lambda))\, d\mu .$$

Make the change of variable $\mu = \lambda + h\upsilon$ and use (A.19) to get

$$\text{(A.21)} \qquad |\Psi_h(\lambda + \tau h) - \Psi_h(\lambda) - \tau h N_h(\lambda)| \le C_0 h^{2-n} \frac{(1+|\tau|)^{n+2} - 1}{n+2} .$$

Now, using (3.6 and 7) and $-i\rho'(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tau \hat{\rho}(\tau)\, d\tau$,

$$\text{(A.22)} \qquad (\Psi_h * \theta_h)(\lambda) - \Psi_h(\lambda) + ih\rho'(0) N_h(\lambda)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} (\Psi_h(\lambda + \tau h) - \Psi_h(\lambda) - \tau h N_h(\lambda)) \hat{\rho}(\tau)\, d\tau .$$

Equation (3.36) follows from (A.21), (A.22) and the fact that $\rho'(0) = 0$. Given Lemma 5.1, this completes the proof of Proposition 5.

Proof of Lemma 5.1: Suppose $\tau \ge 0$. We have three cases.

Case 1: Suppose $h\tau \le \delta_0$, where δ_0 is from (3.8). Then

$$N_h(\lambda + \tau h) - N_h(\lambda) = \int_{\lambda}^{\lambda+\tau h} N'_h(\mu)\, d\mu$$

$$\le C_1 \int \hat{\rho}\left(\frac{\mu - \lambda}{h}\right) N'_h(\mu)\, d\mu$$

$$= 2\pi C_1 h (N'_h * \theta_h)(\lambda),$$

where $C_1 > 0$ so that $\frac{1}{C_1} \leq \rho(\sigma)$ for $\sigma \in [-\delta_0, \delta_0]$. Theorem 2 then says that there is a $C_2 > 0$ such that

$$|N_h(\lambda+\tau h) - N_h(\lambda)| \leq C_2 h^{1-n}$$

for $\lambda \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$ and $h\tau \leq \delta_0$.

Case 2: Suppose $h\tau \geq \frac{\epsilon_0}{2}$. Then, using (3.3),

$$\begin{aligned} |N_h(\lambda+\tau h) - N_h(\lambda)| &\leq |N_h(\lambda+\tau h) + N_h(\lambda)| \\ &\leq C' h^{-n}((\lambda+\tau h)^n + \lambda^n). \end{aligned}$$

Since $h^{-1} \leq \frac{2\tau}{\epsilon_0}$, $h \leq 1$, and $\lambda \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$, there is a constant $C_3 > 0$ such that

$$|N_h(\lambda+\tau h) - N_h(\lambda)| \leq C_3 h^{1-n}(1+|\tau|)^{n+1}.$$

Case 3: Suppose $\delta_0 \leq h\tau \leq \frac{\epsilon_0}{2}$. Choose the integer k so that $k\delta_0 \leq h\tau < (k+1)\delta_0$. Then

$$\begin{aligned} |N_h(\lambda+\tau h) - N_h(\lambda)| \leq\ & |N_h(\lambda+\tau h) - N_h(\lambda+k\delta_0)| \\ &+ \sum_{\ell=0}^{k-1} |N_h(\lambda+(\ell+1)\delta_0) - N_h(\lambda+\ell\delta_0)|. \end{aligned}$$

For $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$, each term above may be bound by Case 1, because $\lambda + \ell\delta_0 \in (\lambda_0-\epsilon_0, \lambda_0+\epsilon_0)$ for each $\ell = 0, 1, \cdots, k$. So in this case,

$$|N_h(\lambda+\tau h) - N_h(\lambda)| \leq k C_2 h^{1-n} \leq \frac{\epsilon_0}{2\delta_0} C_2 h^{1-n}$$

for $\lambda \in (\lambda_0 - \frac{\epsilon_0}{2}, \lambda_0 + \frac{\epsilon_0}{2})$.

Putting the three cases together then gives that there is a $C_0 > 0$ such that (A.19) is true for $\tau \geq 0$. The proof is similar for $\tau \leq 0$.

__Proof of Theorem 6__: If λ_0 is not critical for V, then there is an $\epsilon_0 > 0$ so that no value in $[\lambda_0-\epsilon_0,\lambda_0+\epsilon_0]$ is critical for V.

__Lemma 6.1__: The point {0} is isolated in $\overline{\mathcal{L}_{(\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)}}$.

Given Lemma 6.1, we may find a $\rho \in C_0^\infty(\mathbb{R})$ satisfying (3.8) such that

$$\operatorname{supp} \rho \cap \overline{\mathcal{L}_{(\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)}} = \{0\}.$$

Then Theorems 3 and 4 and Proposition 5 prove Theorem 6.

__Proof of Lemma 6.1__: We must show, for classical periodic trajectories of period $t \neq 0$ and energies in $(\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)$, that there is a $t_0 > 0$ such that $|t| \geq t_0$. This would prove that {0} is isolated in $\overline{\mathcal{L}_{(\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)}}$.

The trajectories obey (A.2) and (A.3). Define, for fixed $(y,\eta) \in \mathbb{R}^{2n}$ with energy $|\eta|^2 + V(y) \in (\lambda_0-\epsilon_0,\lambda_0+\epsilon_0)$

$$D(t) = (x-y)\cdot\xi - (\xi-\eta)\cdot\partial_x V(x).$$

Then $D(t) = 0$ for a periodic trajectory starting at (y,η) and having period t. Since

$$\frac{dD}{dt} \equiv D'(t) = 2|\xi|^2 + |\partial_x V|^2 - (x-y)\cdot\partial_x V + 2(\xi-\eta)\cdot\partial_{xx}V\cdot\xi$$

we see that $D'(0) = 2|\eta|^2 + |\partial_x V(y)|^2 \geq d' > 0$, for some $d' > 0$ depending only on λ_0 and ϵ_0 (otherwise V has a critical point in $[\lambda_0-\epsilon_0,\lambda_0+\epsilon_0]$, contradicting our hypotheses). Furthermore, from (A.3) and (3.2) the trajectory is bounded, and from (3.1) the quantities $|\partial_x V|$ and $\|\partial_{xx}V\|$ are bounded on the trajectory. Using these facts and (A.2), we obtain the lower bound

$$D'(t) \geq D'(0) - d|t|,$$

for some $d > 0$ depending only on λ_0 and ϵ_0. Since

$$D(t) = \int_0^t D'(t)\, dt \geq D'(0)|t| - \frac{1}{2} d|t|^2,$$

we see that the zeroes of $D(t)$ for which $t \neq 0$ obey $|t| \geq t_0 = \frac{2D'(0)}{d} > 0$.

This completes the proof of Lemma 6.1, and hence Theorem 6.

APPENDIX B

The Method of Stationary Phase

In this appendix we review several results on the method of stationary phase which we need in order to evaluate the small h asymptotics of integrals of the form

(B.1) $$\int a(x)e^{i\phi(x)/h}\, d^m x,$$

where $\underline{a} \in C_0^\infty(\mathbb{R}^m)$, $\phi \in C^\infty(\mathbb{R}^m)$ and ϕ is real valued.

Suppose for the moment that $|\nabla\phi| > 0$ on supp $\underline{a}$. If supp $\underline{a}$ is sufficiently small that ϕ may be used as a coordinate in a new coordinate system $\{y_\upsilon(x_1,\ldots,x_m)\}_{\upsilon=1}^m$ over supp $\underline{a}$ (take $y_1(x) = \phi(x)$), then we have

$$\int a(x)e^{i\phi(x)/h}\, d^m x = \int f(y_1)e^{iy_1/h}\, dy_1 = \hat{f}\left(\frac{-1}{h}\right),$$

where $f(y_1) = \int a(x(y)) \left|\frac{\partial(x)}{\partial(y)}\right| dy_2 \cdots dy_m$. Since $f \in C_0^\infty(\mathbb{R})$, we conclude that the integral (1) is $0(h^{+\infty})$ as $h \to 0$. We can always reduce to this case by use of some partition of unity over supp $\underline{a}$.

A result of Hörmander [9], which is proven by clever integrations by parts, gives uniform bounds.

__Theorem__ $\underline{8}$ ([9, Theorem 7.7.1]): Let $K \subset \mathbb{R}^m$ be compact, X an open neighborhood of K, and k a nonnegative integer. If $\underline{a} \in C_0^\infty(K)$, $\phi \in C^\infty(X)$ and ϕ real valued, then

$$\left|\int a(x)e^{i\phi(x)/h}\, dx\right| \le Ch^k \sum_{|\alpha|\le k} \sup|D^\alpha a| \quad |\nabla\phi|^{|\alpha|-2k}$$

for $h > 0$. Here C (which depends on ϕ, but not $\underline{a}$) is bounded when

$\sum_{|\alpha|\leq k+1} |D^{\alpha}\phi|$ stays bounded.

This theorem tells us that (B.1) vanishes rapidly as $h \to 0$ when the phase ϕ has no stationary points in supp $\underline{a}$. By a stationary point of ϕ, we mean that $\nabla\phi = 0$ at that point.

Now consider a simple case wherein the phase ϕ has a stationary point. Let the dimension $m = 1$, put $\phi(x) = \frac{1}{2}x^2$, and let $\underline{a} \in C_0^{\infty}(\mathbb{R})$. The phase ϕ is stationary at $x = 0$. Since the Fourier transform of $e^{ix^2/2h}$ is $(2\pi ih)^{1/2}\, e^{-ih\xi^{2/2}}$, we may compute (B.1)

(B.2) $$\int a(x)e^{ix^2/2h}\,dx = \frac{1}{2\pi}\int \hat{a}(\xi)(2\pi ih)^{1/2} e^{-ih\xi^{2/2}}\,d\xi.$$

Using $\left| e^{it} - \sum_{j=0}^{k-1} (it)^j/j! \right| \leq |t|^k/k!$ for $t \in \mathbb{R}$ in (B.2) gives

(B.3) $$\left| \int a(x)e^{ix^2/2h}\,dx - (2\pi ih)^{1/2} \sum_{j=0}^{k-1} \frac{(-ih/2)^j}{j!}\, a^{(2j)}(0) \right|$$

$$\leq \frac{1}{2\pi}\int \left|\hat{a}(\xi)(2\pi ih)^{1/2}\right| \frac{|-ih\xi^2/2|^k}{k!}\,d\xi$$

$$\leq Ch^{k+\frac{1}{2}} \sum_{j=0}^{2k+1} \|D^j a\|_{L^2},$$

In the right-hand side of (B.3) the following bound was used

$$\int |\hat{a}(z)|\,|\xi|^{2k}\,d\xi = \int |\hat{a}(z)|\,|\xi|^{2k}(1+|\xi|)\,(1+|\xi|)^{-1}\,d\xi$$

$$\leq \left(\int \left|\hat{a}(\xi)(1+|\xi|)^{2k+1}\right|^2 d\xi\right)^{1/2} \left(\int (1+|\xi|)^{-2}\,d\xi\right)^{1/2}$$

$$\leq C' \sum_{j=0}^{2k+1} \left\|\hat{a}(\xi)\xi^j\right\|_{L^2} = C' \sum_{j=0}^{2k+1} \|D^j a\|_{L^2}.$$

So we see from (B.3) that (B.2) is not $0(h^{+\infty})$ as $h \to 0$. This is due to the presence of the point of stationary phase in the integral at $x = 0$. As (B.3) shows, we can compute the small h asymptotic behavior to any order we desire, and the result depends on the value of a and its derivatives at the location of the point of stationary phase.

This last example can be extended to higher dimensions in a straightforward manner, yielding:

Theorem 9 ([9, Theorem 7.7.3]): Let A be an $m \times m$ real symmetric non-degenerate matrix. Then for every integer $k > 0$ and integer $s > m/2$,

$$\left|\int a(x)e^{i\langle x,Ax\rangle/2h}\,dx - S_k(h)\right|$$

$$\leq C_k(\|A^{-1}\|h)^{m/2+k} \sum_{|\alpha|\leq 2k+S} \|D^\alpha a\|_{L^2}$$

for $h > 0$ and where

$$S_k(h) = (2\pi h)^{m/2}\,|\det A|^{-1/2}\,e^{i\pi\,\mathrm{sgn}\,A/4}$$

$$\cdot \sum_{j=0}^{k-1} \frac{(-ih/2)^j}{j!}\,\langle D, A^{-1}D\rangle^j\,a(0).$$

Finally, we consider the more general case where $\phi(x)$ is stationary, but not degenerate, at a point $x = x_0$. Since

$$\phi(x) = \phi(x_0) + \tfrac{1}{2}\langle(x-x_0),\phi''(x_0)(x-x_0)\rangle + g_{x_0}(x),$$

where

(B.4) $$g_{x_0}(x) = \phi(x) - \phi(x_0) - \tfrac{1}{2}\langle(x-x_0),\phi''(x_0)(x-x_0)\rangle.$$

We then write for (1),

$$e^{i\phi(x_0)/h}\int\left\{a(x)e^{ig_{x_0}(x)/h}\right\}e^{i\langle(x-x_0),\phi''(x_0)(x-x_0)\rangle/h}\,dx$$

and apply Theorem 9 (with the quantity in braces replacing a there). One obtains

Theorem 10 ([9, Theorem 7.7.5]): Let $K \subset \mathbb{R}^m$ be compact, X an open neighborhood of K and k a positive integer. If $\underline{a} \in C_0^\infty(K)$, $\phi \in C^\infty(X)$, $\phi'(x_0) = 0$, det $\phi''(x_0) \neq 0$ and $\phi'(x) \neq 0$ for $x \in K \setminus \{x_0\}$, then

$$\text{(B.5)}\quad \left| \int a(x) e^{i\phi(x)/h} dx - (2\pi h)^{m/2} \left|\det \phi''(x_0)\right|^{-1/2} e^{i\pi \operatorname{sgn} \phi''(x_0)/4} \cdot \sum_{j=0}^{k-1} L_j a \right|$$

$$\leq C h^{m/2+k} \sum_{|\alpha| \leq 2k} \sup |D^\alpha a|.$$

Here C stays bounded when $\sum_{|\alpha| \leq 3k+1} \sup|D^\alpha \phi|$ and $\left\| \phi''(x_0)^{-1} \right\|$ stay bounded in X. The $L_j a$ are given by

$$L_j a = \sum_{\substack{\upsilon - \mu = j \\ 2\upsilon \geq 3\mu}} (i^j 2^\upsilon \mu! \upsilon!)^{-1} \langle D, \phi''(x_0)^{-1} D \rangle^\upsilon (g_{x_0}^\mu a)(x_0).$$

There is no problem in extending this to the case where ϕ and hence x_0 may depend on some parameters y [9, Theorem 7.7.6], as long as $\sum_{|\alpha| \leq 3k+1} \sup \left| D_x^\alpha \phi(x,y) \right|$ and $\left\| \phi_{xx}(x_0(y), y)^{-1} \right\|$ stay bounded for $x \in X$ and all y of interest. For reference, we list $L_0 a$ and $L_1 a$ explicitly:

$$\text{(B.6)}\quad \begin{aligned} L_0 a &= a(x_0) \\ L_1 a &= -i\Big\{ \tfrac{1}{2} \langle D, BD \rangle a(x_0) \\ &\quad + \tfrac{1}{2} \langle Da, BD\langle D, BD\rangle \phi \rangle (x_0) \\ &\quad + \tfrac{1}{8} (\langle D, BD \rangle^2 \phi)(x_0)\, a(x_0) \\ &\quad + \tfrac{5}{24} \langle D\langle D, BD\rangle \phi, BD\langle D, BD\rangle \phi \rangle (x_0)\, a(x_0) \Big\}, \end{aligned}$$

where the matrix $B = \phi''(x_0)^{-1}$.

In the proofs of Theorems 2, 3 and 4 we use the results of (B.5) and (B.6).

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