

WKB and the Periodic Table

by
C. Fefferman

In this expository article, I'd like to ~~explain~~^{motivate} some work that Luis Seco and I have done on the ground-state energy of an atom of atomic number $Z \gg 1$. If one ignores relativistic effects, then the mathematical problem is as follows. Fix a nucleus of charge $+Z$ at the origin. If ~~there~~ N electrons are located at $x_1, x_2, \dots, x_N \in \mathbb{R}^3$, then their potential energy is given by

$$V_{\text{Coulomb}}^{NZ}(x_1, \dots, x_N) = -\sum_{k=1}^N \frac{Z}{|x_k|} + \sum_{1 \leq j < k \leq N} \frac{1}{|x_j - x_k|} \quad (1)$$

We regard the electrons as quantized, so that the state of the system is given by a wave function

$$\psi(x_1, \dots, x_N) \in L^2(\mathbb{R}^{3N}).$$

For simplicity, we neglect spin here. (If we had taken spin into account, then ψ would take values in the N -fold tensor power of \mathbb{C}^2 . This changes no ideas, but introduces factors of 2 into some key formulas).

Not every $\psi \in L^2(\mathbb{R}^{3N})$ is allowed as the wave function for N electrons. The requirements on ψ are as follows:

ψ must have norm 1 in $L^2(\mathbb{R}^{3N})$

$\psi(x_1, \dots, x_N)$ must be antisymmetric, i.e.,

$$\psi(x_{\sigma_1}, x_{\sigma_2}, \dots, x_{\sigma_N}) = (\text{sgn } \sigma) \psi(x_1, \dots, x_N) \text{ for permutations } \sigma. \quad (2)$$

The subspace of $L^2(\mathbb{R}^{3N})$ consisting of all functions

satisfying (2) will be called $L^2_{\text{antisymm}}(\mathbb{R}^{3N})$.

The (expected) energy of N electrons in the state ψ is given by $\langle H_{N,Z}\psi, \psi \rangle$, where the inner product is

taken in L^2 , and $H_{N,Z}$ is the Hamiltonian, given by

$$H_{N,Z} = -\sum_{k=1}^N (-\Delta_{x_k}) + V_{\text{Coulomb}}^{N,Z} \quad (3)$$

The ground state energy $E(N, Z)$ of N electrons and a nucleus of charge Z is defined as the lowest eigenvalue (or, more precisely, the infimum of the spectrum) of $H_{N,Z}$ acting on $L^2_{\text{antisymmetric}}(\mathbb{R}^{3N})$.

We may then consider either a neutral atom by taking $E(Z, Z)$, or we may allow nature a chance to force $N \approx Z$ by forming

$$E(Z) = \inf_N E(N, Z). \quad (4)$$

The results known so far are too crude to distinguish these; let us first restrict attention to (4). The mathematical problem we study is to understand the asymptotic behavior of $E(Z)$ for large Z . We want to understand the asymptotics of $E(Z)$ so precisely that we can see small irregularities in its behavior. Let me try to explain why one might care about the small irregularities.

We can get a crude idea of how atoms behave by simply dropping the repulsion term $\sum_{j < k} |x_j - x_k|^{-1}$ from (1), to obtain an easier Hamiltonian $\tilde{H}_{N,Z}$.

Without repulsion, (3) simplifies enormously. In fact, we have

$$\tilde{H}_{N,Z} = \sum_{k=1}^N \left(-\Delta_{x_k} - \frac{Z}{|x_k|} \right) \text{ acting on } L^2_{\text{antisymm.}}(\mathbb{R}^{3N}),$$

which reduces by separation of variables to the Hydrogen atom

$$-\Delta_x - \frac{Z}{|x|} \text{ on } L^2(\mathbb{R}^3). \quad (5)$$

Of course, the eigenvalues and eigenfunctions of (5) are computed explicitly in any quantum mechanics textbook.

If $E_{1,\epsilon} \leq E_{2,\epsilon} \leq E_{3,\epsilon} \leq \dots$ are the eigenfunctions of (5),

counted according to multiplicity, then the lowest eigenvalue of $\tilde{H}_{N,Z}$ is easily seen to be

$$\tilde{E}(N, Z) = E_{1,\epsilon} + E_{2,\epsilon} + \dots + E_{N,\epsilon}. \quad (6)$$

In fact, the eigenvalues of (5) are $-\frac{Z^2}{4n^2}$,

with multiplicity n^2 ($n=1, 2, 3, \dots$). If we had taken spin into account, then we would have found that the multiplicity of $-\frac{Z^2}{4n^2}$ is $2n^2$, and ~~from~~ for the next

few paragraphs we work with E_1, E_2, E_3, \dots given by

$$E_k = -\frac{Z^2}{4n^2} \quad \text{for } N(n) \leq k \leq N(n+1), \quad (7)$$

where $N(0) = 0$, $N(n+1) - N(n) = 2n^2$.

With E_k and $\tilde{E}(N, Z)$ given by (6), (7), one computes easily the energy asymptotics of a neutral atom:

$$\tilde{E}(Z, Z) \approx -(\text{const}) Z^{7/3} \quad \text{for large } Z. \quad (8)$$

Note that $\tilde{E}(Z, Z)$ has small irregularities as a function of Z . In fact, one checks easily that

$Z^{-2} \tilde{E}(Z, Z)$ is a piecewise linear function of Z , whose slope changes at the atomic numbers

$Z = N(n)$. Thus, the atomic numbers at which $E(Z, Z)/Z^2$ exhibits a kink are

$$Z = 2, 10, 28, \dots \quad (9)$$

Now $Z=2$ and $Z=10$ are the atomic numbers of Helium and Neon, the first two noble gases. It is natural to believe that detailed properties of $E(Z, Z)$ affect chemical reactions, since chemical binding arises from the small difference in ground-state energy between, say, ~~two~~ a diatomic molecule and two isolated atoms. Note that $Z=28$ is the wrong prediction for the next noble gas (Argon; $Z=18$). However, we have done amazingly well, considering that we dropped the electron repulsion in (1)

The realization that an oversimplified atom, without electron repulsion, leads to something like the periodic table goes back to Niels Bohr.

Since the 1920's, physicists and mathematicians have worked to understand the asymptotics of $E(Z, Z)$ and of $E(N, Z)$ with the electron repulsion taken into account. See [FS3] for a brief historical discussion. ~~The main points that we understand so far are as follows~~

The main points that we understand so far are as follows. For large Z , both $E(Z)$ and $E(Z, Z)$ are given by

$$E(Z) = -c_0 Z^{7/3} + c_1 Z^2 - c_2 Z^{5/3} + o(Z^{5/3}) \quad (10)$$

for explicit, positive constants c_0, c_1, c_2 . To derive this, one ~~uses~~ relates (3) to an effective one-electron Hamiltonian

$$H = -\Delta_x + Z^{4/3} V_{TF}(Z^{1/3}|x|) \quad \text{on } L^2(\mathbb{R}^3), \quad (11)$$

where $V_{TF}(y)$ is a universal function on $(0, \infty)$, defined as the solution of an explicit ordinary differential equation with boundary conditions. The most painful part of the proof of (10) is to ~~derive~~ derive a precise asymptotic formula for the sum of the negative eigenvalues of (11) by refined WKB theory.

~~The main points that we understand so far are as follows. For large Z , both $E(Z)$ and $E(Z, Z)$ are given by~~
 ~~$E(Z) = -c_0 Z^{7/3} + c_1 Z^2 - c_2 Z^{5/3} + o(Z^{5/3})$~~
~~for explicit, positive constants c_0, c_1, c_2 . To derive this, one~~
~~relates (3) to an effective one-electron Hamiltonian~~
 ~~$H = -\Delta_x + Z^{4/3} V_{TF}(Z^{1/3}|x|)$ on $L^2(\mathbb{R}^3)$,~~
~~where $V_{TF}(y)$ is a universal function on $(0, \infty)$,~~
~~defined as the solution of an explicit ordinary differential equation with boundary conditions.~~
~~The most painful part of the proof of (10) is to~~
~~derive a precise asymptotic formula for the sum of the negative eigenvalues of (11) by~~
~~refined WKB theory.~~

Seco and I have understood (11) well enough to conjecture an asymptotic formula for the irregular variations in the sum of the negative eigenvalues of (11), as a function of Z . We believe our formula can be proven with enough hard work, using the ideas in our papers [FS 1...8]. We believe further that this can be used to understand the irregularities in $E(Z)$ for very large Z . It is, however, far from clear that our asymptotic analysis applies to Z as low as 100, and thus has anything to do with chemistry. The prediction of chemical binding energies from quantum mechanics by rigorous mathematics remains a very hard problem. ~~It is~~

In this article, ~~we~~ I've tried to motivate some mathematics, but have not even tried to explain the statements of the results. The interested reader may get a good idea of what is involved by reading the old survey paper [L] and the ~~int~~ introductions to our papers [FS 2...8]. See also [IS] for an important result on the ground-state energy of a molecule.

REFERENCES

- [FS1] C. Fefferman and L. Secco, The ground-state energy of a large atom,
Bull. A.M.S. 23 (2), (1990), 525-530.
- [FS2] _____, Eigenvalues and eigenfunctions of ordinary
differential operators, Adv. Math. 95 (1992), 145-305
- [FS3] _____, On the Dirac and Schwinger corrections to the ground
state energy of an atom, Adv. Math. 107 (1994), 1-185
- [FS4] _____, The density in a one-dimensional potential,
Adv. Math. 107 (2) (1994) 187-364
- [FS5] _____, The eigenvalue sum for a one-dimensional potential,
Adv. Math. 108 (2) (1994) 263-335
- [FS6] _____, Aperiodicity of the Hamiltonian flow in the
Thomas-Fermi potential, Rev. Math. Iberoam. 9 (3) (1993) 409-551
- [FS7] _____, The density in a three-dimensional radial potential,
Adv. Math. 111 (1) (1995) 88-161
- [FS8] _____, The eigenvalue sum for a three-dimensional radial
potential, Adv. Math. 119 (1) (1996) 26-116
- [IS] V. Ivrii and I.M. Sigal, On the asymptotics of large
Coulomb systems, Annals of Math.
- [L] E. Lieb, Thomas-Fermi and related theories of atoms and molecules,
Rev. Mod. Phys. 53 (4) (1981), 603-641