Advanced Mathematical Quantum Mechanics

Mathematisches Institut der LMU – SS2009
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Individual project no. 1:
The Thomas–Fermi–von Weizsäcker energy functional

✓ Work out individually the details of the problem outlined in the scheme below.

✓ Results and techniques discussed in the class as well as in the tutorial sessions and in the weekly homeworks will be needed.

✓ Questions, info, further clarifications: Alessandro, usual times and places.

✓ Please return your completed project by June, Wednesday 3.

Part 1. [*Definition, domain, lowest energy*] Define the Thomas-Fermi-von Weizsäcker[1] functional $\mathcal{E}^{\mathrm{TFW}}$ as[2]

$$\mathcal{E}^{\mathrm{TFW}}(\rho) \;:=\; A\int[\nabla\rho^{1/2}(x)]^2\mathrm{d}x+\frac{\gamma}{p}\int\rho(x)^p\mathrm{d}x+\int V(x)\rho(x)\mathrm{d}x+D(\rho,\rho) \tag{1}$$

with the standard notation of the Thomas-Fermi theory. Here $A>0$ is a constant that is adjustable to reproduce a certain desired physical behaviour [3] and since the values of A and γ will not have relevance here, set $A=\gamma=1$. To let some interesting dependence of $\mathcal{E}^{\mathrm{TFW}}(\rho)$ vs p to emerge, $p>1$ is treated as a parameter. Clearly, if $p=5/3$ then $\mathcal{E}^{\mathrm{TFW}}$ has the form of $\mathcal{E}^{\mathrm{TF}}$ plus the von Weizsäcker correction. Furthermore,

$$V(x)=-\sum_{i=k}^{K}\frac{z_k}{|x-R_k|} \tag{2}$$

with the standard notation of the Thomas-Fermi theory. As a natural domain for $\mathcal{E}^{\mathrm{TFW}}(\rho)$ consider the space

$$\mathcal{D} \;:=\; \left\{\,\rho\mid\rho(x)\geqslant 0,\ \rho^{1/2}\in H^1\cap L^{2p}\,\right\}. \tag{3}$$

[1]The Thomas-Fermi theory of atoms, attractive because of its simplicity, is not satisfactory because it yields an electron density with incorrect behaviour very close and very far from the nucleus. Moreover, it does not allow for the existence of molecules. In order to correct this, in 1935 von Weizsäcker suggested the addition of an inhomogeneity correction $\int[\nabla\rho^{1/2}]^2$ to the kinetic energy. Unlike the TF equation, in the corresponding Euler equation for TFW the pointwise relation between ϕ and ρ is lost, which makes the TFW theory more difficult mathematically. However, the physical consequences of the TFW theory are much richer and *qualitatively* parallel to the physics of real atoms and molecules. Although this problem sheet will cover only some basic features of the TFW theory, it has to be emphasized that such a theory remedies the following defects of the TF theory. First, ρ will be finite at the nuclei. Second, binding of atoms occurs and negative ions are stable (these two facts are closely related). Moreover, ρ has exponential fall off if $\lambda<\lambda_c$. Last, the TFW theory provides the Z^2 correction to the energy.

[2]all integrals on $\mathbb{R}^3$, as usual

[3]originally A was taken to be $\hbar^2/(2m)$, whereas the value $0.186\hbar^2/(2m)$ turns out to be the optimum to give the the Z^2 energy correction

1.1) As an equivalent expression for $\mathcal{D}$ show that $\rho \in \mathcal{D}$ is the same as $\rho \geqslant 0$, $\rho \in L^1 \cap L^p$, and $\nabla\rho^{1/2} \in L^2$.

1.2) Prove that $\mathcal{D}$ is convex and that $\rho \mapsto \mathcal{E}^{\mathrm{TFW}}(\rho)$ is strictly convex.

1.3) For any $\lambda > 0$ define

$$E(\lambda) \;:=\; \inf\left\{\, \mathcal{E}^{\mathrm{TFW}}(\rho) \mid \rho \in \mathcal{D},\ \int \rho = \lambda \,\right\}. \tag{4}$$

Prove that

$$E(\lambda) \;=\; \inf\left\{\, \mathcal{E}^{\mathrm{TFW}}(\rho) \mid \rho \in \mathcal{D},\ \int \rho \leqslant \lambda \,\right\}. \tag{5}$$

and that $\lambda \mapsto E(\lambda)$ is convex and monotone non increasing.

Part 2. [*Minimiser*]

2.1) Prove that for every $\varepsilon > 0$ there exists a constant C_ε, depending on V but independent of ρ, such that

$$\left| \int V(x)\rho(x)\mathrm{d}x \right| \;\leqslant\; \varepsilon\|\rho\|_3 \;+\; C_\varepsilon D(\rho,\rho)^{1/2} \tag{6}$$

for every $\rho \geqslant 0$.

2.2) Deduce from the above conclusion and by means of the Sobolev inequality that there are positive constants a, b such that

$$\mathcal{E}^{\mathrm{TFW}}(\rho) \;\geqslant\; a\big(\, \|\rho\|_3 \;+\; \|\rho\|_p^p \;+\; \|\nabla\rho^{1/2}\|_2^2 \;+\; D(\rho,\rho)\,\big) \;-\; b \tag{7}$$

2.3) Take a minimising sequence $\{\rho_n\}_{n=1}^{\infty}$ for $\mathcal{E}^{\mathrm{TFW}}(\rho)$, i.e.,

$$\int \rho_n(x)\mathrm{d}x \leqslant \lambda \qquad \text{and} \qquad \mathcal{E}^{\mathrm{TFW}}(\rho_n) \xrightarrow{n\to\infty} E(\lambda)\,. \tag{8}$$

Prove that up to passing a subsequence there exists $\rho_\lambda \in \mathcal{D}$ such that

$$\liminf \int [\nabla\rho_n^{1/2}]^2 \mathrm{d}x \;\geqslant\; \int [\nabla\rho_\lambda^{1/2}]^2 \mathrm{d}x \tag{9}$$

$$\liminf \int \rho_n^p \mathrm{d}x \;\geqslant\; \int \rho_\lambda^p \mathrm{d}x\,. \tag{10}$$

In addition, using the Rellich-Kondrashev theorem[4] prove that, up to passing to a further subsequence, (9) and (10) still hold and

$$\rho_n(x) \;\longrightarrow\; \rho_\lambda(x) \quad \text{almost everywhere.} \tag{11}$$

2.4) Using (11) and Fatou's lemma, prove that

$$\liminf D(\rho_n,\rho_n) \;\geqslant\; D(\rho_\lambda,\rho_\lambda)\,. \tag{12}$$

[4] Theorem 5.1 and Corollary 5.2 in handout no. 10 "Variational Principle" of the previous course "Mathematical Quantum Mechanics", Winter Semester 2008-2009

2.5) Prove that for the sequence determined in point 2.3 and 2.4 above one has

$$\int V(x)\rho_n(x)\mathrm{d}x \xrightarrow{n\to\infty} \int V(x)\rho_\lambda(x)\mathrm{d}x\,. \tag{13}$$

2.6) Prove that $\mathcal{E}^{\mathrm{TFW}}(\rho_\lambda) = E(\lambda)$, i.e., ρ_λ is a minimiser for the TFW functional.

2.7) Prove that the minimiser ρ_λ is unique.

2.8) Notice that (12) is proved here differently than in the class for the analogous statement in the TF energy functional. Explain for which exponents p the simpler proof given in the class works in this case, thus providing an alternative proof of (12) for the TFW theory. Moreover, explain for which p the strategy used in the class for proving (12) without Fatou can be extended to a generalised TF functional on $L^1\cap L^p$ (instead of $L^1\cap L^{5/3}$).

Part 3. [*Minimiser and* λ_c] Define [5]

$$\lambda_c \;:=\; \sup\Big\{\,\lambda\,|\,E(\lambda)=\lim_{\mu\to\infty}E(\mu)\,\Big\}\,. \tag{14}$$

Prove that there exists a minimising $\rho\in\mathcal{D}$ with $\int\rho=\lambda$ if and only if $\lambda\leqslant\lambda_c$. Moreover, prove that when $\lambda>\lambda_c$ the minimiser determined on Part 2 above is ρ_{λ_c}. Last, prove that the function $\lambda\mapsto E(\lambda)$ is *strictly* convex on $[0,\lambda_c]$.

Part 4. [*TFW equation*] Let $p>1$, $\lambda>0$, and

4.1) Introduce the functional

$$\widetilde{\mathcal{E}}^{\mathrm{TFW}}(\xi) \;:=\; \int|\nabla\xi(x)|^2+\frac{1}{p}\int\xi(x)^{2p}\mathrm{d}x+\int V(x)\xi(x)^2\mathrm{d}x+D(\xi^2,\xi^2) \tag{15}$$

on the domain

$$\widetilde{\mathcal{D}} \;:=\; \{\psi:\mathbb{R}^3\to\mathbb{R}\,|\,\psi\in H^1\cap L^{2p}\}\,. \tag{16}$$

Show that if $\xi\in\widetilde{\mathcal{D}}$ then $\xi^2\in\mathcal{D}$ and $\mathcal{E}^{\mathrm{TFW}}(\xi^2)=\widetilde{\mathcal{E}}^{\mathrm{TFW}}(\xi)$.

4.2) For any $\lambda>0$ define

$$\widetilde{E}(\lambda) \;:=\; \inf\Big\{\,\widetilde{\mathcal{E}}^{\mathrm{TFW}}(\xi)\,|\,\xi\in\widetilde{\mathcal{D}},\;\int\xi^2\leqslant\lambda\,\Big\} \tag{17}$$

and prove that $\widetilde{E}(\lambda)=E(\lambda)$.

4.3) Let ρ_λ be the minimiser of $\mathcal{E}^{\mathrm{TFW}}$ on $\mathcal{D}$ with $\int\rho\leqslant\lambda$ (see Part 2). Define

$$\psi \;:=\; \rho_\lambda^{1/2} \tag{18}$$

and

$$\varphi \;:=\; -V-\frac{1}{|x|}*\psi^2\,. \tag{19}$$

Prove that ρ_λ satisfies the equation

$$-\Delta\psi+\psi^{2p-1} = \varphi\,\psi \tag{20}$$

in the sense of distributions, which goes under the name of the *Thomas-Fermi-von Weizsäcker equation.*

[5] although it is not proved here, it turns out that $0<\lambda_c<\infty$.