Variational methods in quantum chemistry and materials science

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Abstract

The concentration compactness principle is a general heuristic variational method due to P. L. Lions. In [1], [2], [3] and [4], P. L. Lions gives various application examples, but none of the minimization problems considered there has a coupled system of multiple constraints on several functions. The goal of this thesis is to examine a concrete example of a family of minimization problems having such a system of constraints with regard to the concentration compactness principle. However, in doing this, it is not clear in advance whether and how the concentration compactness principle is applicable.

Minimization problem

$$\min_{\psi\in\mathcal{A}_K} \underbrace{\int_{\mathbb{R}^6} \frac{1}{2}|\nabla\psi(x,y)|^2 dxdy + \int_{\mathbb{R}^6} (v(x)+v(y))|\psi(x,y)|^2 dxdy + \int_{\mathbb{R}^6} \frac{1}{|x-y|}|\psi(x,y)|^2 dxdy}_{=:\mathcal{E}(\psi)} \quad (1)$$

$(K \in \mathbb{N})$

where $v(x) = -\frac{2}{|x|}$ and the admissible set $\mathcal{A}_K$ is the set of all functions $\psi : \mathbb{R}^6 \to \mathbb{C}$ such that

$$\psi(x,y) = \sum_{i=1}^{K} c_i\phi_i(x)\phi_i(y)$$

with

$$\phi_i : \mathbb{R}^3 \to \mathbb{C}\ ,\ \phi_i \in H^1(\mathbb{R}^3),\quad <\phi_i,\phi_j>_{L^2(\mathbb{R}^3)} = \delta_{ij}\ ,\ c_i \in \mathbb{C}\ ,\ \sum_{i=1}^{K}|c_i|^2 = 1.$$

Two step approach

We want to rewrite the energy functional $\mathcal{E}$ in (1):

Let $\psi : \mathbb{R}^6 \to \mathbb{C}$, $\psi(x,y) = \sum_{i=1}^{K} c_i\phi_i(x)\phi_i(y)$ be admissible for (1). Then

$$\begin{aligned}\mathcal{E}(\psi) &= \sum_{i=1}^{K}\int_{\mathbb{R}^3}|c_i|^2\,|\nabla\phi_i(x)|^2\,dx + 2\sum_{i=1}^{K}\int_{\mathbb{R}^3}|c_i|^2 v(x)|\phi_i(x)|^2 dx \;+ \\ &+ \sum_{i,j=1}^{K}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{c_i\overline{c_j}\phi_i(x)\phi_i(y)\overline{\phi_j}(x)\overline{\phi_j}(y)}{|x-y|}dxdy \\ &=: \mathcal{E}^{(c)}(\phi)\ (\phi = (\phi_1,...,\phi_K)).\end{aligned}$$

Here we have used several times that

$$\int_{\mathbb{R}^3}\phi_i(x)\overline{\phi_j}(x)dx = \delta_{ij}.$$

Now, let us consider the following minimization problems:

$$\min_{\phi\in K_{\mathsf{Id}}}\mathcal{E}^{(c)}(\phi)\ (2)$$

$(c \in \mathbb{C}^K)$
where

$$K_{\mathsf{Id}} := \left\{\phi \in H^1(\mathbb{R}^3)^K \middle|\ <\phi_i,\phi_j>_{L^2(\mathbb{R}^3)} = \delta_{ij}\ \forall i,j = 1,...,K\right\}$$

(Id denotes the identity matrix in $\mathbb{C}^{K\times K}$).

Our approach to (1) is first to examine (2) for arbitrary, but fixed $c = (c_1,...,c_K) \in \mathbb{C}^K$ such that $\sum_{i=1}^{K}|c_i|^2 = 1$, and then to vary c.

The following proposition encourages us to do so:

Proposition 1. *If (2) admits a minimizer for every choice of $c_1,...,c_K \in \mathbb{C}$ such that $\sum_{i=1}^{K}|c_i|^2 = 1$, then the original problem (1) has a solution.*

Main result

We examine the minimization problem (2) for $c \in \mathbb{C}^K$ arbitrary, but fixed, by using the concentration compactness principle due to P.L. Lions.

Applying the concentration compactness principle means following the general heuristic principle given in section I in [1]. In doing this, we have to devise and work out the proofs by ourselves.

We first embed (2) into a family of minimization problems

$$\min_{\phi\in K_G}\mathcal{E}^{(c)}(\phi)\quad (G = (G_{ij})_{i,j=1,...,K} \in \mathcal{M}),$$

where

$$\mathcal{M} := \left\{G \in \mathbb{C}^{K\times K}\middle|\ \overline{G}^T = G,\ 0 \le G \le \mathsf{Id}\right\}$$

and

$$K_G := \left\{\phi = (\phi_1,...,\phi_K) \in H^1(\mathbb{R}^3)^K \middle|\ <\phi_i,\phi_j>_{L^2(\mathbb{R}^3)} = G_{ij}\ \forall i,j = 1,...,K\right\}.$$

This special embedding is motivated by the following lemma stated and proved in [5]:
Lemma: The weak closure of K_{Id} in $H^1(\mathbb{R}^3)^K$ is a subset of the set $\left\{\phi \in H^1(\mathbb{R}^3)^K \middle|\ \exists G \in \mathcal{M}:\ \phi \in K_G\right\}$.

For $G \in \mathcal{M}$ define

$$I_G^{(c)} := \inf\left\{\mathcal{E}^{(c)}(\phi)\middle|\ \phi \in K_G\right\} \text{ and } I_G^{(c),\infty} := \inf\left\{\mathcal{E}^{(c),\infty}(\phi)\middle|\ \phi \in K_G\right\}$$

where

$$\mathcal{E}^{(c),\infty}(\phi) := \sum_{i=1}^{K}\int_{\mathbb{R}^3}|c_i|^2\,|\nabla\phi_i(x)|^2\,dx \;+\; \sum_{i,j=1}^{K}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{c_i\overline{c_j}\phi_i(x)\phi_i(y)\overline{\phi_j}(x)\overline{\phi_j}(y)}{|x-y|}dxdy.$$

Let $C_K := \{i \in \{1,...,K\}|\ c_i \neq 0\}$. Define

$$\mathcal{M}^{(c)} := \{G = (G_{ij})_{i,j} \in \mathcal{M}|\ G_{ij} = 0 = G_{ji}\ \forall i \in \{1,...,K\}\setminus C_K,\ j = 1,...,K\}$$

and

$$\mathbb{1} := \mathbb{1}^{(c)} = (\mathbb{1}_{ij}^{(c)})_{i,j} \in \mathbb{C}^{K\times K} \text{ by } \mathbb{1}_{ij}^{(c)} := \begin{cases}\delta_{ij}, & \text{if } i \in C_K\\ 0, & \text{else}\end{cases}.$$

If $(\phi_n = (\phi_{n,1},...,\phi_{n,K}))_{n\in\mathbb{N}}$ is a sequence in $H^1(\mathbb{R}^3)^K$, we call the sequence $(\phi_{n,i})_{n\in\mathbb{N}}$ in $H^1(\mathbb{R}^3)$ the i-th component of $(\phi_n)_{n\in\mathbb{N}}$.

Now, we state the main result of the thesis:

Theorem 2. *The condition*

$$I_{\mathbb{1}}^{(c)} < I_G^{(c)} + I_{\mathbb{1}-G}^{(c),\infty} \text{ for all } G \in \mathcal{M}^{(c)},\ G \notin \{(G_{ij})_{i,j}|\ G_{ii} = 1\ \forall i \in C_K\}\ (3)$$

is necessary and sufficient for the relative compactness in $H^1(\mathbb{R}^3)$ of all i-th components such that $i \in C_K$ of all minimizing sequences of (2).
In particular, if (3) holds, then (2) has a solution.

References

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