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Monotonicity properties of the quantum mechanical particle density

Dedicated to Professor Hellmut Baumgärtel

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Abstract

An elementary proof of the anti-monotonicity of the quantum mechanical particle density with respect to the potential in the Hamiltonian is given for a large class of admissible thermodynamic equilibrium distribution functions. In particular the zero temperature case is included.

1 Introduction

The Kohn-Sham system of Density Functional Theory, see e.g. [15, 13, 3], has become a widely used tool in the simulation of the electronic structure of matter since it was introduced by Kohn and Sham in 1965 [9]. This was acknowledged by awarding the Nobel prize for Chemistry in 1998 to Walter Kohn [8]. On the other hand there are few mathematical investigation of the Kohn-Sham system up to now: The interesting question of bifurcation of solutions has been treated in [14]. For the Kohn-Sham system as a nonlinear system of partial differential equations on a bounded spatial domain existence of solutions and a priori estimates have been proved, see [6], [7]. The proof for the Kohn-Sham system *with* an exchange–correlation term rests on the existence (and regularity properties) of an unique solution for the corresponding Schrödinger–Poisson system with only self-consistent electrostatic interaction. The underlying fundamental result is the anti-monotonicity of the quantum mechanical particle density with respect to the potential in the Hamiltonian. This was observed in 1990 independently by Nier [12] and Caussignac et al. [1], and is closely related to the convexity of von Neumann-type trace functionals [11, chapter V.3], [10], [5].

In this note we prove in an elementary way the anti-monotonicity of the quantum mechanical particle density with respect to the potential in the Hamiltonian. Thus, we additionally enlarge the class of admissible thermodynamic equilibrium distribution functions used for the composition of the quantum mechanical particle density.

2 Results

In the following $\mathfrak{H}$ is an infinite dimensional, separable Hilbert space with scalar product $(\cdot,\cdot)$, and H is a self-adjoint operator on $\mathfrak{H}$ with compact resolvent.

Theorem 2.1. *Let U and V be bounded, self-adjoint operators on $\mathfrak{H}$. If $f : \mathbb{R} \to \mathbb{R}$*

is a function such that $f(H+U)$ and $f(H+V)$ are trace class operators, then

$$\begin{aligned}&\operatorname{tr}([f(H+U)-f(H+V)][U-V])\\&=\sum_{k,l=1}^{\infty}|(\psi_k,\zeta_l)|^2(f(\lambda_k)-f(\mu_l))(\lambda_k-\mu_l),\end{aligned}\tag{1}$$

where $\{\lambda_k\}_{k=1}^{\infty}$ and $\{\mu_l\}_{l=1}^{\infty}$ are the sequences of eigenvalues (counting multiplicity) of the operators $H+U$ and $H+V$, respectively, and $\{\psi_k\}_{k=1}^{\infty}$, $\{\zeta_l\}_{l=1}^{\infty}$ are the corresponding sequences of (normalised) eigenvectors.

Remark 2.2. *In contrast to previous results (see e.g. [5]) Theorem 2.1 does* not *require that the distribution function f is continuous or (Lebesgue) measurable. This is due to the fact that all occurring spectral measures E are discrete and, hence, all (scalar) measures $(E(\cdot)\varphi,\varphi)$ are purely atomic. Consequently, every function $f:\mathbb{R}\to\mathbb{R}$ is measurable with respect to measures $(E(\cdot)\varphi,\varphi)$ with $\varphi\in\mathfrak{H}$, see e.g. [2, chapter 13.18]. Thus, the integrals $\int_{\mathbb{R}} f(\lambda)\,d(E(\lambda)\varphi,\varphi)$ are well defined for all $\varphi\in\mathfrak{H}$.*

In particular, the characteristic function of the negative half axis is an admissible distribution function. This case corresponds to a quantum system at zero temperature.

Corollary 2.3. *Under the assumptions of Theorem 2.1: If there are real numbers ϵ_U and ϵ_V such that the operators $f(H+U-\epsilon_U)$, and $f(H+V-\epsilon_V)$ are nuclear and, additionally, satisfy*

$$\operatorname{tr}(f(H+U-\epsilon_U))=\operatorname{tr}(f(H+V-\epsilon_V)),\tag{2}$$

then

$$\begin{aligned}&\operatorname{tr}([f(H+U-\epsilon_U)-f(H+V-\epsilon_U)][U-V])\\&=\textstyle\sum_{k,l=1}^{\infty}|(\psi_k,\zeta_l)|^2\quad[f(\lambda_k-\epsilon_U)-f(\mu_l-\epsilon_V)]\,[\lambda_k-\epsilon_U-\mu_l+\epsilon_V]\,.\end{aligned}\tag{3}$$

These results have consequences for the quantum mechanical particle density. Let us assume that H is a semi-bounded, self-adjoint operator with compact resolvent in $L^2(\Omega)$, where Ω is a bounded Lipschitz domain in the up to three dimensional space $\mathbb{R}^d$. In particular, H can be a Schrödinger operator. The operator H is perturbed by a bounded, self-adjoint multiplication operator U induced by a real potential U from $L^\infty(\Omega)$. Then $H+U$ has also a compact resolvent, and we denote by $\{\lambda_k(U)\}_{k=1}^{\infty}$ and $\{\psi_k(U)\}_{k=1}^{\infty}$ the sequences of eigenvalues and (normalised) eigenfunctions of $H+U$ counting multiplicity.

$$\mathcal{N}(U)\stackrel{\text{def}}{=}\sum_{k=1}^{\infty}f(\lambda_k-\epsilon_U)|\psi_k(U)|^2\tag{4}$$

is the quantum mechanical particle density associated with the potential U with respect to the free Hamiltonian H and the thermodynamic equilibrium distribution function f. If there is Fermi-Dirac distribution, then, in the three-dimensional case ($d = 3$) at positive temperature, f is the Fermi function $f(s) = 1/(1 + exp(-s))$. If the sum $\sum_{k=1}^{\infty} f(\lambda_k - \epsilon_U)$ converges, then the (non-linear) particle density operator $\mathcal{N}$ is a map from $L^\infty(\Omega)$ to $L^1(\Omega)$. The normalising shift ϵ_U is the Fermi level defined by

$$N = \int_\Omega \mathcal{N}(U)(x)\,dx = \sum_{k=1}^{\infty} f(\lambda_k - \epsilon_U), \tag{5}$$

where N is total number of particles confined in Ω. If f is not strictly monotone, then the Fermi level is not necessarily uniquely determined by (5). However, we call any solution of (5) a Fermi level of the quantum system.

Corollary 2.4. *Let H be a semi-bounded, self-adjoint operator in $L^2(\Omega)$ and $\{\lambda_k\}_{k=1}^{\infty}$ the sequence of its eigenvalues counting multiplicity. If the distribution function $f : \mathbb{R} \to \mathbb{R}_+$ is monotonously decreasing and obeys*

$$\sum_{k=1}^{\infty} |f(\lambda_k + \alpha)| < \infty \qquad \text{for any real number } \alpha, \tag{6}$$

then the particle density operator (4) is anti-monotone from $L^\infty(\Omega)$ to $L^1(\Omega)$, i.e.

$$\int_\Omega (\mathcal{N}(U)(x) - \mathcal{N}(V)(x))(U(x) - V(x))\,dx \le 0 \tag{7}$$

for all real potentials U, $V \in L^\infty(\Omega)$.

Remark 2.5. *Corollary 2.4 can be extended to more general perturbations U, V than just bounded ones. If, e.g. H and f are chosen such that $f(H + W)X$ is nuclear for all multiplication operators W and X induced by functions from $L^2(\Omega)$, then the (extended) mapping*

$$L^2(\Omega) \ni W \to -\mathcal{N}(W) \in L^2(\Omega)$$

is also monotone, see [6], [7], [5].

3 Proofs

For the proof of our results we need the following simple facts on the summability of double sums $\sum_{k,l=1}^{\infty} a_{kl}$. We say the double sum converges if the sequence $\{A_n\}_{n=1}^{\infty}$ of partial sums $A_n = \sum_{k,l=1}^{n} a_{kl}$ converges. If $\sum_{k=1}^{\infty}\sum_{l=1}^{\infty} |a_{kl}|$ converges, then $\sum_{k,l=1}^{\infty} a_{kl}$ is summable, the sums $\sum_{k=1}^{\infty}\sum_{l=1}^{\infty} a_{kl}$ and $\sum_{l=1}^{\infty}\sum_{k=1}^{\infty} a_{kl}$ converge, and

$$\sum_{k,l=1}^{\infty} a_{kl} = \sum_{k=1}^{\infty}\sum_{l=1}^{\infty} a_{kl}, = \sum_{l=1}^{\infty}\sum_{k=1}^{\infty} a_{kl}, \tag{8}$$

see [4, Theorem XI.5.2].

Proof of Theorem 2.1

Because H is a self-adjoint operator with compact resolvent in the separable Hilbert space $\mathfrak{H}$ the operators $H+U$ and $H+V$ also have a compact resolvent. Since $f(H+U)$ and $f(H+V)$ are trace class operators, there is

$$\begin{aligned}&\operatorname{tr}((f(H+U)-f(H+V))\,(U-V))\\&\quad=\operatorname{tr}(f(H+U)(U-V))-\operatorname{tr}(f(H+V)(U-V)).\end{aligned}$$

The trace can be expressed in terms of an eigensystem:

$$\begin{aligned}&\operatorname{tr}(f(H+U)(U-V))\\&\quad=\sum_{k=1}^{\infty}(f(H+U)(U-V)\psi_k,\psi_k)=\sum_{k=1}^{\infty}f(\lambda_k)((U-V)\psi_k,\psi_k),\end{aligned}$$

where the sum on the right-hand side is absolutely convergent. Further, one can develop each ψ_k into a Fourier series with respect to the system $\{\zeta_l\}_{l=1}^{\infty}$:

$$\psi_k=\sum_{l=1}^{\infty}(\psi_k,\zeta_l)\zeta_l.$$

Hence,

$$\begin{aligned}&\operatorname{tr}(f(H+U)(U-V))\\&\quad=\sum_{k=1}^{\infty}f(\lambda_k)((U-V)\psi_k,\psi_k)=\sum_{k=1}^{\infty}f(\lambda_k)\sum_{l=1}^{\infty}\overline{(\psi_k,\zeta_l)}((U-V)\psi_k,\zeta_l).\end{aligned}$$

As the sum $\sum_{k=1}^{\infty}|f(\lambda_k)|\sum_{l=1}^{\infty}\left|\overline{(\psi_k,\zeta_l)}((U-V)\psi_k,\zeta_l)\right|$ converges, (8) implies

$$\operatorname{tr}(f(H+U)(U-V))=\sum_{k,l=1}^{\infty}f(\lambda_k)\overline{(\psi_k,\zeta_l)}((U-V)\psi_k,\zeta_l).$$

Next we note

$$((U-V)\psi_k,\zeta_l)=([(H+U)-(H+V)]\psi_k,\zeta_l)=(\lambda_k-\mu_l)(\psi_k,\zeta_l)$$

for all k, $l\in\mathbb{N}$. Hence,

$$\begin{aligned}\operatorname{tr}(f(H+U)(U-V))&=\sum_{k,l=1}^{\infty}f(\lambda_k)\overline{(\psi_k,\zeta_l)}(\lambda_k-\mu_l)(\psi_k,\zeta_l)\\&=\sum_{k,l=1}^{\infty}f(\lambda_k)(\lambda_k-\mu_l)|(\psi_k,\zeta_l)|^2.\end{aligned}\tag{9}$$

Similarly one gets

$$\operatorname{tr}(f(H+V)(U-V))=\sum_{k,l=1}^{\infty}f(\mu_l)(\lambda_k-\mu_l)|(\psi_k,\zeta_l)|^2,$$

which, together with (9), implies (1).

Proof of Corollary 2.3

From (2) one gets

$$\operatorname{tr}\left(f(H+U-\epsilon_U)-f(H+V-\epsilon_V)\right)[\epsilon_V-\epsilon_U]=0,$$

and consequently

$$\begin{aligned}&\operatorname{tr}\left([f(H+U-\epsilon_U)-f(H+V-\epsilon_V)][U-V]\right)\\ =\;&\operatorname{tr}\left([f(H+U-\epsilon_U)-f(H+V-\epsilon_V)][(U-\epsilon_U)-(V-\epsilon_V)]\right).\end{aligned}$$

Now, Theorem 2.1, applied to $\tilde{U}=U-\epsilon_U$ and $\tilde{V}=V-\epsilon_V$, implies the relation (3).

Proof of Corollary 2.4

One has to check that for any U, $V\in L^\infty$ the relation (7) holds. First, one verifies that $f(H+W-\epsilon_W)$ is a trace class operator for any bounded operator W. Indeed, there is

$$H-\|W\|-|\epsilon_W|\le H+W-\epsilon_W$$

in the sense of forms. Due to the minimax principle, the monotone decay of the distribution function f, and the supposition (6) the operator $f(H+W-\epsilon_W)$ is trace class. Thus, the series (4) converges in $L^1(\Omega)$. By straightforward calculations one verifies that the expression on the left hand side of (7) equals (3). As f decreases monotonously, the pre-factors

$$\left(f(\lambda_k-\epsilon_U)-f(\mu_l-\epsilon_V)\right)\left((\lambda_k-\epsilon_U)-(\mu_l-\epsilon_V)\right)$$

are all non-positive, what proves the assertion.

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