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The Theorem of Hohenberg and Kohn for Subdomains of a Quantum System

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The theorem of Hohenberg and Kohn is extended to subdomains of a bounded quantum system. It is shown that the ground state particle density of an arbitrary subdomain uniquely determines the ground state properties of this subdomain, of any other subdomain, and of the total domain of the system.

Key words: Theorem of Hohenberg and Kohn – Subdomains of a quantum system – Particle density – Ground state properties.

1. Introduction

In recent years there has been a considerable interest in the general properties of subdomains of a quantum mechanical system (molecular fragments, unit cells in crystals) [1–5]. The principal aim of such a work is an understanding of the properties of the total system in terms of the properties of its parts. Of particular interest in this context is the question to what extent the particle density of a sudomain determines the physical properties of the subdomain, or even of the whole domain of the system.

There is an important theorem by Hohenberg and Kohn [6] saying that (under certain restrictions) the ground state wave function and energy of a quantum mechanical system are unique functionals of the spin-averaged particle density. In

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the case of a one-particle system it was further shown [4] that this theorem holds also for virial fragments, which are specially defined subdomains of the physical space of the system. In this context it has been conjectured [2, 3] that a similar theorem could also be true for the virial fragments of a many particle system.

In the present article we are able to show that the theorem of Hohenberg and Kohn does hold for subdomains of a bounded (or periodic) many particle system. More precisely: we will show, that the ground state particle density of an *arbitrary* subdomain of a quantum system enclosed in a bounded domain uniquely determines the wave function, the energy and more generally, the expectation value of any spin-free observable associated with that particular subdomain, or with any other subdomain or with the total domain of the system.

Our proof is based on certain regularity conditions for the potentials appearing in the Hamiltonian, and on a rigorous analysis of the proof of the original theorem of Hohenberg and Kohn, which will show that these regularity conditions are in fact also necessary for the proof given by Hohenberg and Kohn (i.e. for the case, where the whole domain of the system is considered).

2. Analysis of the Proof of the Theorem of Hohenberg and Kohn

For the proof of this theorem (which is valid also for an infinitely extended quantum system) we have to make the following general mathematical assumptions, which are from the physical point of view not very restrictive:

(a) For concreteness we are dealing with an N-electron system. Generalisations to arbitrary Fermion or Boson systems are entirely trivial. All wave functions considered in this note are therefore elements of the subspace of all antisymmetric functions of the complex Hilbert space $L_2(G) \otimes f_1 \otimes f_2 \cdots \otimes f_N$. G denotes the N-fold direct sum of an arbitrary bounded or unbounded simply connected region g in R^3, f_i the spin space of the ith electron. The Hamiltonian has to be totally symmetric with regard to particle permutations and may contain spin operators.
(b) The Hamiltonian H of the system has to be self-adjoint, bounded from below, and below a certain point the spectrum of the Hamiltonian H has to be discrete. Furthermore, the Hamiltonian has to be elliptic with coefficients analytic everywhere except on a set of measure zero with connected complement G_0 in G. It is well known [7, 8] that the usual, non-relativistic and spin-free Born–Oppenheimer Hamiltonian (involving Coulomb singularities) fulfils these conditions.
(c) Except for permissible degeneracy due to time-inversion invariance (e.g. the Kramers degeneracy in the case of an odd number of electrons) the ground state of the Hamiltonian has to be non-degenerate.
(d) We write the Hamiltonian H in the form $H = K + V$, where V is a sum of real and local one-electron potentials,

$$V(r_1, \ldots, r_N) = \sum_{n=1}^{N} v(r_n).$$

Remark. These assumptions warrant the validity of the following prerequisites actually used for the proof of the theorem of Hohenberg and Kohn: there exists a non-degenerate ground state; this ground state is uniquely determined by the variational principle and does not vanish except on a set of measure zero.

We shall give the proof for the case of a non-degenerate ground state only. If there is a degeneracy e.g. due to time-inversion symmetry the proof applies to a symmetry adapted subspace of the Hilbert space. The final result remains unchanged because the potential and the charge density are invariant under time-inversion.

Notation. We consider two Hamiltonians $H_1 = K + V_1$ and $H_2 = K + V_2$ with the corresponding normalized ground-state wave functions ϕ_1, ϕ_2, and eigenvalues E_1, E_2. The ith particle coordinate $x_i = (r_i, s_i)$ stands for the position vector r_i and the spin variable s_i.

Lemma 1. $\phi_1 = \alpha\phi_2$ if and only if $V_1 = V_2 + \beta$ (α and β are constants, $|\alpha| = 1, \alpha \in \mathbb{C}, \beta \in R$).

Proof. (a) If $\phi_1 = \alpha\phi_2 = \phi$, then $H_1\phi = E_1\phi$ and $H_2\phi = E_2\phi$, hence by subtraction $(V_1 - V_2)\phi = (E_1 - E_2)\phi$. By assumption the Hamiltonian is elliptic with analytic coefficients in G_0, hence (compare e.g. Ref. [9]) ϕ is analytic in G_0. From this analyticity follows (compare e.g. Ref. [10]) that $\phi \neq 0$ in G_0 except on a set of measure zero. Hence $V_1 - V_2 = E_1 - E_2$ except on a set of measure zero.
(b) If $V_1 = V_2 + \beta$, then the Hamiltonians H_1 and $H_2 = H_1 - \beta$ have the same eigenspaces. By assumption ϕ_1 and ϕ_2 belong to the non-degenerate lowest eigenvalue (of H_1, H_2 respectively), hence ϕ_1 and ϕ_2 span the same 1-dimensional eigenspace.

We define the spin-averaged particle-density by

$$n_k(r) = N \sum_{s_1} \cdots \sum_{s_N} \int_g d^3r_2 \cdots \int_g d^3r_N |\phi_k(rs_1, r_2s_2, \ldots, r_Ns_N)|^2, \; k = 1, 2$$

Lemma 2. $n_1(r) \neq n_2(r)$ if and only if $v_1(r) \neq v_2(r) + \text{const}$.

Proof. (a) If $v_1 \neq v_2 + \text{const.}$, then according to Lemma 1 $\phi_1 \neq \alpha\phi_2$. Our general assumptions on the structure of the Hamiltonian warrant the validity of the variational principle, hence

$$E_1 = (\phi_1|H_1|\phi_1) < (\phi_2|H_1|\phi_2) = E_2 + (\phi_2|V_1 - V_2|\phi_2),$$

or

$$E_1 < E_2 + \int_g d^3r[v_1(r) - v_2(r)]n_2(r).$$

The strict inequality sign is important and due to the fact that E_1 is non-degenerate. In the same way we find

$$E_2 < E_1 + \int_g d^3r[v_2(r) - v_1(r)]n_1(r),$$

hence by addition:

$$0 < \int_g d^3r[v_1(r) - v_2(r)][n_2(r) - n_1(r)].$$

$n_2 = n_1$ would imply $0 < 0$, hence $n_1 \neq n_2$.
(b) Conversely $n_1 \neq n_2$ implies $\phi_1 \neq \alpha\phi_2$ (because evidently $\phi_1 = \alpha\phi_2$ implies $n_1 = n_2$). Hence according to Lemma 1 $v_1 = v_2 + \text{const.}$

From Lemma 2 it immediately follows that the energy and the ground state wave function (and hence all expectation values of spin-free observables) are unique functionals of the particle density $n(r)$ (theorem of Hohenberg and Kohn). (According to Lemma 2 equal particle densities $n_1(r)$, $n_2(r)$ imply equal potentials $v_1(r)$, $v_2(r)$ (up to a constant β), i.e. equal Hamiltonians H_1, H_2 (up to the constant β), and hence equal ground state energies E_1, E_2 (if $\beta = 0$, i.e. if the origin of the energy is the same in both cases). Further, from a combination of Lemma 1 and Lemma 2 one obtains $n_1(r) = n_2(r)$ if and only if $\phi_1 = \alpha\phi_2$).

It is important to remark that the conditions of analyticity and connectedness used to prove Lemma 1 are essential to exclude the case, where ϕ_1, ϕ_2 are equal to zero on a subdomain D, which is not of measure zero, but are different from zero elsewhere. In such a case we could not exclude the situation, where $v_1 - v_2$ is different from $E_1 - E_2$ on D (and hence on G_0).

In the case of a one-electron system Lemma 1 alone leads to the theorem of Hohenberg and Kohn, since ϕ has no nodes and therefore it is uniquely (up to a phase factor) determined by $n(r)$.

For practical purposes the usefulness of the theorem of Hohenberg and Kohn is restricted by the fact, that the unique functionals of the density $n(r)$ are unknown in general, and further, because not any reasonable looking function is a possible particle density $n(r)$ of a quantum mechanical system. Hence, for a formulation of a variational principle or for the definition of a functional derivative $\delta/\delta n(r)$ we have to impose subsidiary conditions. For example, the particle density has to be N-representable. For Bosons there is no restriction, but for Fermions $n(r)$ must be derivable from a 1-density operator that is an element of the so-called Thomas space (compare Coleman [11]).

3. The Case of a Subdomain

We consider now a subdomain Ω of the physical three-dimensional domain g of the system. Let $n_{1\Omega}(r)$, $n_{2\Omega}(r)$ be the restrictions of $n_1(r)$, $n_2(r)$ to Ω. We first prove, that $n_{1\Omega} = n_{2\Omega}$ implies $n_1 = n_2$. This last statement is true, if we can show, that $n_1(r)$, $n_2(r)$ are analytic in g almost everywhere.

To sketch this proof we remark that, since $\phi(r_1s_1, r_2, s_2, \ldots, r_Ns_N)$ is analytic in G except on the set S of singular points, this is also true for

$$n(r_1, r_2, \ldots, r_N) = N \sum_{s_1} \cdots \sum_{s_N} |\phi(r_1s_1, r_2s_2, \ldots, r_Ns_N)|^2.$$

We further recall that $n(r_1, r_2, \ldots, r_N)$ is an integrable function in $G \subset R^{3N}$, hence it is integrable on the subspace of $N-1$ variables r_i.

We now consider the typical case of a Born–Oppenheimer Hamiltonian with Coulomb interactions between the particles. Here the set S of singular points is the union of sets M_{ij} defined by $r_i = r_j$, $i, j = 1, 2, \ldots, N$, $i \neq j$ (due to the Coulomb singularities of the electron–electron interactions) and sets $M_{i\alpha}$ defined by $r_i = R_\alpha$, $i = 1, 2, \ldots, N$ (from the Coulomb singularities of the interaction between the electrons and the nuclei at their fixed positions R_α, $\alpha = 1, 2, \ldots, f$). Therefore, for any fixed value r_i, the set S is of measure zero in the $(3N-3)$-dimensional subspace of the remaining $N-1$ variables and therefore does not cut this subspace into two disjoint parts with non-analytic common boundary. (These properties follow also directly from the assumptions made in Sect. 2).

We now make the additional assumption, that the physical region g of the system is an arbitrary large but *bounded* three-dimensional domain. Since an analytic function, integrated over a finite domain of a subset of its variables, gives an analytic function of the remaining variables, it follows (together with the properties of $n(r_1, r_2, \ldots, r_N)$ discussed before) that

$$n(r) = N \int n(r, r_2, r_3, \ldots, r_N)\, d^3r_2\, d^3r_3 \cdots d^3r_N$$

is analytic in g except on the singular points R_α.

Thus $n(r)$ is a unique functional of n_Ω. From this result it follows together with the theorem of Hohenberg and Kohn, that also the ground state energy E, the ground state wave function $\phi(x_1, x_2, \ldots, x_N)$ and therefore the restriction of ϕ to any $3N$-dimensional subset of G are unique functionals of $n_\Omega(r)$. Hence all expectation values of spin-free operators defined by ϕ or by means of such restrictions of ϕ are unique functionals of $n_\Omega(r)$.

As an example consider the energy $E_{\Omega'}$ of a subdomain $\Omega' \subseteq g$ (Ω' may or may not coincide with the original subdomain Ω). We write the spin-free Hamiltonian of the system in the form

$$H = \sum_{i=1}^{N} H^{(1)}(r_i) + \sum_{\substack{i<j\\1}}^{N} H^{(2)}(r_i, r_j),$$

where $H^{(1)}(r_i)$ and $H^{(2)}(r_i, r_j)$ are one- and two-particle operators respectively. The energy $E_{\Omega'}$ may be defined as (cf. Ref. [2–4])

$$E_{\Omega'} = \int_{\Omega'} [H^{(1)}(r_1')\Gamma^{(1)}(r_1, r_1')]_{r_1'=r_1}\, d^3r_1$$

$$+ \int_{\Omega'} d^3r_1 \int_g H^{(2)}(r_1, r_2)\Gamma^{(2)}(r_1, r_2; r_1, r_2)\, d^3r_2.$$

From the definitions of $\Gamma^{(1)}$ and $\Gamma^{(2)}$, the one- and two-particle density matrices, it is immediately clear, that both integrals in Eq. (1) can be expressed by means of the following restrictions of ϕ

$$\phi_{\Omega'}(x_1, x_2, \ldots, x_i, \ldots, x_N)$$
$$= \phi(r_1, s_1; r_2, s_2, \ldots, r_i, s_i, \ldots, r_N, s_N)\big|_{r_i \in \Omega', r_k \in g, k \neq i}.$$

Therefore $E_{\Omega'}$ is a unique functional of $n_\Omega(r)$. This is of course also true for each of the different energy terms (kinetic, electron-electron repulsive, . . .) contained in $E_{\Omega'}$.

4. Summary

In this article we have shown, that the ground state particle density $n_\Omega(r)$ of an arbitrary subdomain Ω of a quantum system which is contained in a finite domain $g \subset R^3$ uniquely determines all the (spin-free) ground state properties in Ω, in any other subdomain Ω', and in the total domain g of the system (provided Ω, Ω' and g are of the same dimension).

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