Degeneracy in Density Functional Theory: Topology in $\nu$- and $n$-Space

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This paper clarifies the topology of the mapping between $\nu$- and $n$-space in fermionic systems. Density manifolds corresponding to degeneracies $\nu = 1$ and $\nu > 1$ are shown to have the same mathematical measure: every density near a $\nu$-ensemble-$\nu$-representable ($\nu$-VR) $n(r)$ is also $\nu$-VR (except “boundary densities” of lower measure). The role of symmetry and the connection between $T = 0$ and $T = 0^+$ are discussed. A lattice model and the Be-series are used as illustrations.

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Density functional theory (DFT) of electrons in an external potential $v(r)$ uses the ground-state density $n(r)$ as basic variable [1]. $n(r)$ uniquely determines $v(r)$ (apart from a constant); conversely, for a given number, $N$, of electrons, $v(r)$ obviously determines $n(r)$ uniquely if and only if the ground state is non-degenerate. These facts point to the interesting role of degeneracy in the mapping $v(r) \Longleftrightarrow n(r)$.

In 1982-3, Levy [3] and Lieb [4] discovered examples of well-behaved density functions, $n(r)$, which could not be reproduced as non-degenerate, non-interacting ground-state densities of any $v(r)$, and were called non-$\nu$-representable (non-VR). In these examples, the $n(r)$ could be reproduced as weighted averages of densities of degenerate ground states corresponding to a $v(r)$.

Soon afterwards, Kohn [5] adopted a lattice version of the Schrödinger equation, $r \rightarrow r_l$ ($l = 1, \ldots, M$), in which $v(r)$ and $n(r)$ become $v_l$ and $n_l$ and can be viewed as $M'$-dimensional ($M'$-D) vectors: $\vec{v} \equiv (v_1, \ldots, v_M')$, with $M' = M - 1$, $v_M = 0$; and $\vec{n} \equiv (n_1, \ldots, n_M')$, with $n_M = N - (n_1 + \ldots + n_M')$. The $M'$ lattice points are enclosed by boundary points on which $\vec{v} = +\infty$ and, accordingly, all wave functions vanish. It was shown in [5] that in the $M'$-D $\vec{n}$-space there are finite $M'$-D regions in which all “points” (densities) are VR.

In 1985, Chayes et al. (CCR) [6], using a similar lattice model, proved the following important result: Any well-behaved $\vec{n}$ ($0 < n_l \leq 1$) can be uniquely represented as weighted average of $\nu$ degenerate ground-state densities associated with a $\vec{v}$. We call the special case $\nu = 1$-VR, and the general case ($\nu \geq 1$) $\nu$-VR. Thus, $\vec{n}$-space is filled by manifolds $S^\nu\nu$, in each of which $\vec{n}$ is $\nu$-VR. Each $S^\nu\nu$ maps on a corresponding manifold $Q^\nu\nu$ in $\vec{v}$-space.

This paper aims at an understanding of the topologies of the regions $S^\nu\nu$ and $Q^\nu\nu$ and of the nature of the boundaries between them. This has mathematical and physical significance, e.g. in the search for self-consistent solutions of Kohn-Sham (KS) equations [6]. We shall see that $\nu$-VR densities with $\nu > 1$ are not mathematically exceptional and, in particular, do not depend on symmetries of the potential. As illustrations we shall present a finite lattice model and the Be-series for $Z \rightarrow \infty$ [5]. We also discuss the relationship between $T = 0$ ensembles and $T = 0^+$ thermal ensembles. We limit ourselves to systems that are everywhere nonmagnetic.

Interior regions in $\vec{n}$-space. We first recapitulate Ref. [3] for $1$-VR densities, and then generalize to $\nu$-VR.

a) $\nu = 1$. Since there is a non-degenerate non-interacting ground state with a finite gap, corresponding to some $\vec{v}$, we can use non-degenerate perturbation theory to calculate the first-order density change, $1n_l$, due to a weak perturbing potential $1v_l$:

$$1n_l = \sum_{l=1}^{M'} \chi_{ll'}^{-1} v_{l'} , \quad l = 1, \ldots, M' .$$

Since, according to [3], the density $\vec{n}$ of a non-degenerate ground state uniquely determines $\vec{v}$ (no arbitrary constant since $v_M = 0$), the homogeneous set of equations corresponding to [3] has no solution other than $1v_{l'} \equiv 0$, so that [3] can be inverted:

$$1v_l = \sum_{l'=1}^{M'} \chi_{ll'}^{-1} n_{l'} , \quad l = 1, \ldots, M' .$$

Thus, any first-order change of $\vec{n}$ preserving $N$ produces a density which is also 1-VR. This is the case in the entire $M'$-D neighborhood surrounding the point $\vec{n}$, in which $\Delta$ remains positive.

b) $\nu > 1$ [6]. We denote by $\Psi_1, \ldots, \Psi_\nu$ a set of $\nu$ orthogonal degenerate ground-state wave functions corresponding to $i^\nu\nu$, with common energy $E$ and finite gap $\Delta$. The remaining eigenfunctions are $\Psi_{\nu+1}, \ldots$. What conditions must be imposed on infinitesimal $[O(\lambda)]$ potential changes $1\vec{v}$ which will preserve this degeneracy? In the space of the $\Psi_j$, the perturbed Hamiltonian matrix is

$$H_{ij} = E_i \delta_{ij} + 1V_{ij} \quad i, j = 1, 2, \ldots ,$$

$$E_i = E \langle i | = 1, \ldots, g \rangle , \quad E_i \geq E + \Delta \quad (i \geq g+1) ,$$

and $1V_{ij} = \sum_{l=1}^{M'} \langle i | 1v_l | j \rangle$. Because of the finite $\Delta$, the off-diagonal $1V_{ij}$ with $i \leq g$ and $j \geq g + 1$, or vice versa, can be removed to all orders in $\lambda$ by orthogonal transformations leading to the decoupled $g \times g$ block Hamiltonian

$$\tilde{H}_{ij} = E\delta_{ij} + 1V_{ij} + O(\lambda^2) \quad i, j = 1, \ldots, g .$$
Diagonalization by an orthogonal transformation $T_{ij} = \delta_{ij} + \epsilon t_{ij} + O(\lambda^2)$ and the requirement that the eigenvalues remain degenerate gives a transformed Hamiltonian

$$
\hat{H}_{ij} \equiv \left(T^{-1}\hat{H}T\right)_{ij} = (E + \epsilon\delta_{ij} + O(\lambda^2)).
$$

(5)

On inverting the transformation and noting that every matrix commutes with $\delta_{ij}$, one finds $\hat{H}_{ij} = \hat{H}_{ij} + O(\lambda^2)$.

Comparison with Eq. (4) leads to $\frac{1}{2} (g - 1)(g + 2)$ conditions of equal diagonal and vanishing off-diagonal $1^n_{ij}$.

Thus, every point $\vec{n}$ with a $g$-fold degenerate ground state and finite $\Delta$ is embedded in a manifold in $\vec{v}$-space of dimension $D^g = [M' - \frac{1}{2}(g - 1)(g + 2)]$, in which the degeneracy $g$ and a finite $\Delta$ are preserved. Ground-state degeneracies in $\vec{v}$-space are “rare” in the above sense.

Each $\vec{n}$ gives rise to a set of ensemble densities,

$$
\vec{n} = \sum_{j=1}^{g} w_j \vec{n}_j, \quad 0 < w_j \leq 1, \quad \sum_{j=1}^{g} w_j = 1,
$$

(6)

with $\vec{n}_j = \vec{n}_j (R^g \Psi_j)$, where $R^g$ is a $g$-D orthogonal transformation $\left[\frac{1}{2}g(g - 1)\right]$ parameters] and the $w_j$ are normalized weights $(g - 1)$ parameters]. Thus, all $\vec{n}$ in a finite $M'$-D neighborhood enclosing a $g$-VR $\vec{n}$, defined by $\Delta(\vec{n}) > 0$ and $w_j > 0$, are also $g$-VR: Degeneracy in $\vec{n}$-space is not “rare”.

Boundary surfaces in $\vec{n}$-space. Except for boundaries of $D \leq M' - 1$, $\vec{n}$-space is completely filled by $M'$-D regions $S^g$, with degenerate ground-state levels and a finite positive gap to the nearest excited state.

Apart from “corners” ($D \leq M' - 2$), interior regions $S^g$ in $\vec{n}$-space are bounded by $(M' - 1)$-D internal and external “surfaces” $\Sigma^g$, see Fig. 1. Each internal $\Sigma^g$ separates two interior regions $S'$ and $S^{g+1}$. A point $\vec{n}$ on such a $\Sigma^g$ corresponds to a $(g + 1)$-fold degenerate ground state but with one of the $g + 1$ weights equal to zero. On the $g$-side of $\Sigma^g$ there is a $g$-fold degeneracy and a small gap to the $(g + 1)$-state opens up from 0. On the $(g + 1)$-side there is a $(g + 1)$-fold degeneracy and one of the $g + 1$ weights starts from 0 and becomes positive.

External boundaries correspond to either one of the $n_l$ becoming zero, reflecting particle conservation; or one of the $n_l$ becoming 1, reflecting the Pauli principle. For examples of both kinds, see the lattice model below.

Imposed symmetry conditions. Consider a Hamiltonian, invariant under a group $G$ of the lattice with irreducible representations $h$ with $D = g_h$. Let the ground state have total degeneracy $g = \sum h_m g_h$ due to $m_h$ occurrences of $h$. If a small perturbation $H'$ respecting the group $G$ is imposed, how many further conditions must be met by $H'$ so that the degeneracy is maintained?

We have shown above that the perturbation must have vanishing off-diagonal matrix elements (MEs) between all degenerate ground states, and equal diagonal MEs.

Off-diagonal MEs. The symmetry of $H'$ assures immediately that all off-diagonal MEs between $h \neq h'$ vanish
where, for fcc lattices, \( \nabla_l^2 f_l = [\sum_k f_k - 12f_l]/a^2 \), with \( k \) running over the nearest neighbors of lattice site \( l \). Energies and potentials will be measured in units of \( 2ma^2/h^2 \).

We consider cases of \( C_{4h} \) symmetry: \( v_l \equiv V_1 (V_2) \), \( l = 1-8; \) \( v_l \equiv V_2, l = 9-12; \) \( v_{13} = 0 \). The lattice wave functions belong to the following representations of \( C_{4h} \): \( \Gamma_l \equiv A_g \) (s-like), \( E_g \) and \( A_u \) (p-like), \( B_2 \) (d-like), and \( B_3 \) (f-like). \( A_g \) occurs three times \( (1A_g, 2A_g, 3A_g) \), \( E_u \) occurs twice \( (1E_u, 2E_u) \), all other representations occur only once. The eigenfunctions and energies required solutions of 3-, 2- and 1-D secular equations.

Consider the ground state of 2 non-interacting spinless fermions. The lowest level is always \( 1A_g \) (1s-like). The next level depends on \( V_1 \) and \( V_2 \), see Fig. 3. The \( (V_1, V_2) \) plane divides into three distinct, infinitely extended regions (shown in yellow), in each of which the eigenfunction of the second level belongs to a particular irreducible representation of \( C_{4h} \): region 1a, \( 1A_u \) (2p_x-like); region 1b, \( 2A_g \) (2s-like); and region 1c, \( 1E_u \) (2p_x, 2p_y-like). In each region, the ground state is non-degenerate (not counting degeneracies dictated by symmetry, such as in the 2-D representation \( 1E_u \)).

On the boundary lines 2a, 2b and 2c (shown in blue), crossings of levels belonging to different representations of \( C_{4h} \) occur, leading to two-fold (accidental) degeneracies. Along 2a, the potential has cubic symmetry \( (V_1 = V_2) \), and the two lowest p-like levels \( (1A_u, 1E_u) \) coincide. On 2b, the \( 2A_g \) and \( 1A_u \) levels cross, and on 2c, the \( 2A_g \) and \( 1E_u \) levels cross. All three boundary lines meet in a single point, “3”, at \( V_1 = V_2 = 8 \). At this point only, the ground state has a three-fold accidental degeneracy. Note that the degeneracies on 2b and 2c are not due to additional potential symmetries.

As shown above, a ground state with restricted symmetry maintains its degeneracy if \( \sum m/n (m/n - 1)/2 + m/n \equiv 1 \) conditions are met. In the present example, \( m/n = 1 \) always. Regions 2a, 2b, 2c are therefore lines (1 condition), region 3 is a point (2 conditions) in the \( (V_1, V_2) \)-plane.

We now discuss all \( n \) with \( C_{4h} \) symmetry. Like \( v \), they are fully characterized by two values, \( N_1 \) and \( N_2 \), the total density at points 1–8 and 9–12. \( n_{13} = 2 - N_1 - N_2 \). \( N_1 \) and \( N_2 \) are confined within a stripe in the \( (N_1, N_2) \) plane, with an “inner” boundary, with \( n_{13} = 1 \), reflecting the Pauli principle \( (N_1 + N_2 < 1 \) would imply \( n_{13} > 1 \) \), and an “outer” boundary, with \( n_{13} = 0 \), reflecting particle conservation \( (N_1 + N_2 \leq 2) \).

The manifold of allowed densities in the \( (N_1, N_2) \) plane is subdivided into different regions, corresponding to those of the \( (V_1, V_2) \)-plane. All of the regions in the \( (N_1, N_2) \) plane have \( D = 2 \). This is in line with our general topological results for g-VR densities.

Fig. 4 illustrates the highest occupied state along paths in the \( (V_1, V_2) \) and \( (N_1, N_2) \) planes (see dotted lines in Fig. 3 top and bottom): \( 1A_u \) with weight 1 (region 1a), \( 1E_u \) with weight 1 (equal-weight combination of 2p_x, 2p_y-like states; region 1c), or a linear combination of the degenerate \( 1A_u \) and \( 1E_u \) (region 2a), with fractional weights.

Physical Example: the Be-series. Be has a nominal electronic configuration \( (1s)^2(2s)^2 \) and a term value \( ^1S \). Without interactions, \( 2s \) and \( 2p \) are degenerate. The Be-series consists of neutral Be (\( Z = 4 \)), and
there is no unoccupied degenerate state. Under these lar, there must be a finite range in $1/\lambda$.

For a given low temperature, $\beta^{-1} \ll \Delta$, the canonical density corresponding to $\vec{v} \searrow 0$ is given by

$$n' = \frac{1}{Z} \sum e^{-\beta E_j} n(\vec{r}^2 \Phi_j) + O(\lambda) + O(e^{-\beta \Delta}),$$

where $Z = \sum e^{-\beta E_j}$. This density is equal, to leading order, to the density $\vec{n}$ of Eq. (\ref{eq:n}), if $1/\beta$ is chosen so that $\vec{r}^2 \Phi_j = \Psi_j$ and $Z^{-1} e^{-\beta \vec{E}} = w_j$. As $\beta \Delta \to \infty$, $1/\beta \sim \beta^{-1} \to 0$ and $n' \to n$. This establishes the correspondence between ensemble densities at $T = 0$ and canonical densities at low temperatures, $\beta \Delta \gg 1$.

Concluding remarks. The problem of $\nu$-representability \cite{Bunge} had cast a shadow of uncertainty over DFT, which was very largely clarified in \cite{Baerends}. Here, building on CCR, we clarify the topology of the $\nu(\vec{r})$-$n(\vec{r})$ mapping. The Be-series and a lattice model are used for illustration. The transition from a dense discrete lattice, $\nu_1$, to a continuous variable, $\nu$, does not appear to offer difficulties. An open issue is extension to spin magnetism.

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