Tilted-Plane Structure of the Energy of Finite Quantum Systems

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The piecewise linearity condition on the total energy with respect to the total magnetization of finite quantum systems is derived using the infinite-separation-limit technique. This generalizes the well-known constancy condition, related to static correlation error, in approximate density functional theory. The magnetic analog of Koopmans' theorem in density functional theory is also derived. Moving to fractional electron count, the tilted-plane condition is derived, lifting certain assumptions in previous works. This generalization of the flat-plane condition characterizes the total energy surface of a finite system for all values of electron count N and magnetization M. This result is used in combination with tabulated spectroscopic data to show the flat-plane structure of the oxygen atom, among others. We find that derivative discontinuities with respect to electron count sometimes occur at noninteger values. A diverse set of tilted-plane structures is shown to occur in d-orbital subspaces, depending on chemical coordination. General occupancy-based total-energy expressions are demonstrated thereby to be necessarily dependent on the symmetry-imposed degeneracies.

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Density functional theory (DFT), a workhorse of computational chemistry and condensed matter physics [1–3], owes its success to the development of relatively efficient, reliable, and accurate approximations to the exchange-correlation (XC) functional [4–11]. These approximations can be developed by enforcing exact conditions and appropriate norms on a functional of given mathematical form [12]. Two well-known such exact conditions are the piecewise linearity condition with respect to electron count N [13] and the constancy condition with respect to spin-magnetization (henceforth referred to as magnetization for concision) M [14,15] that, as we will discuss, is a special case of a more general linearity condition. The former condition states that the total ground state energy of a system with external potential $v(\mathbf{r})$ and electron count $N = N_0 + \omega$ is given by

$$E_v(N_0+\omega) = (1-\omega)E_v(N_0) + \omega E_v(N_0+1), \quad (1)$$

where $N_0 \in \mathbb{N}^0$ and $0 \leq \omega \leq 1$ [13,14,16]. A DFT calculation for a finite system with a noninteger electron count necessitates fractional occupancy of at least one Kohn Sham (KS) orbital. Assuming this fractional occupancy is limited to one KS orbital, the slope of the linear segment of the $E_v(N)$ curve is given by

$$\left(\frac{\partial E_v}{\partial N}\right)_v = \epsilon_{\mathrm{f}}, \quad (2)$$

where ϵ_{f} is the fractionally occupied KS eigenvalue [17–20]. A derivative discontinuity must therefore occur at integer values of electron count [21–26], at least. The left-hand partial such derivative is given by the highest occupied KS eigenvalue. The right-hand partial derivative is given by the lowest unoccupied KS eigenvalue, ϵ_{LUKS}, with an additional contribution from the derivative discontinuity of the exact XC functional, that is by

$$\lim_{\delta\to 0^+} \left(\frac{\partial E_v}{\partial N}\right)_v \bigg|_{N_0+\delta} = \epsilon_{\mathrm{LUKS}} + \Delta^N_{\mathrm{xc}}. \quad (3)$$

The piecewise linearity condition with respect to electron count [13], as given by Eq. (1), follows from the convexity condition [27], namely that

$$2E_v[N_0] \leq E_v[N_0-1] + E_v[N_0+1]. \quad (4)$$

The second of the two aforementioned exact conditions is the constancy condition with respect to magnetization M [14,15], which states that the total ground state energy of a system with electron count N_0 and magnetization M satisfies, for any magnetization $|M| \leq M_0$,

$$E_v(N_0, M) = E_v(N_0, M_0) = E_v(N_0, -M_0). \quad (5)$$

Here, $M_0 \in \mathbb{N}^0$ is the maximum magnetization of the lowest-energy state for a given integer electron count $N_0 \in \mathbb{N}^0$. $E_v(N, M)$ denotes the ground state energy of the system with specified electron count N and magnetization M, noting that these are independent parameters in DFT, subject to $|M| \leq N$. Here, and in what follows, it is supposed that no ambient field coupling to spin is present.

The linearity and constancy conditions given by Eqs. (1) and (5) have been combined and generalized [14,28–37] to give the flat-plane condition

$$E_v(N, M) = (1-\omega)E_v(N_0, M_0) + \omega E_v(N_0+1, M_1) \tag{6}$$

for $|M| \leq M_0 + \omega(M_1 - M_0)$, where $N = N_0 + \omega$ and $M_1 \in \mathbb{N}^0$ is the maximum magnetization of the lowest-energy state for the $N_0 + 1$ electron system.

Many approximate XC functionals violate these exact conditions, and this failure has been directly linked to poor performance in the prediction of band gaps [38–40], molecular dissociation [41–44], and electronic transport [45]. A small number of functionals enforce, fully or to some extent, the flat-plane condition [37,46–56].

It has long been recognized in the literature that the constancy condition with respect to magnetization and the accompanying flat-plane condition apply only to the aforementioned limited interval of magnetization states. In previous works to generalize this, X. Yang *et al.* [36] proposed the existence of two types of flat planes, for example, and Gál and Geerlings [34] proposed a piecewise linearity condition for magnetization by invoking a zero-temperature grand canonical ensemble.

In this Letter, we rigorously classify the $E_v[N, M]$ surface for all values of magnetization M, as opposed to the limited interval $|M| \leq M_0 + \omega(M_1 - M_0)$, across all formulations of DFT that satisfy three minimum requirements. These are that the total energy functional is (a) exact for all v-representable spin densities, (b) size-consistent, which is connected to the idea of nearsightedness, and (c) translationally invariant. We derive a piecewise linearity condition with respect to magnetisation (Theorem 1) and an accompanying, general "tilted-plane" condition (Theorem 2). A tilted plane may have a nonzero partial derivative with respect to both N and M, while a flat plane [as defined by Eq. (6)] can only have a nonzero partial derivative with respect to N. In certain cases only, the tilted plane simplifies to the well-known flat plane.

Theorems 1 and 2 are exact conditions for the XC functional, and so may inform and stimulate the development of improved XC approximations. They highlight the opportunity for functionals that incorporate explicit derivative discontinuities with respect to electron count N and magnetization M. Theorem 1 opens a new avenue for incorporating spin-polarized atomic reference data as guidance for spin-polarized functional generalizations [57–59]. Furthermore, these two theorems demonstrate that occupancy-based functionals, such as in DFT+U type methods [46,47,49,60–63] and certain machine-learning based methods [64–66], might beneficially take on different analytical expressions depending on symmetry-imposed degeneracies, as we approach exactitude.

In Supplemental Material (SM) [67], Sec. IV, Corollary 1.1 provides the analog of the DFT Koopmans' condition for spin, i.e., an exact condition on the spin splitting of the effective (e.g., Kohn-Sham) potential. In spin-polarized systems, this splitting underpins the prediction of magnetic excitations and exchange couplings from a DFT starting point.

Theorem 2 classifies the $E_v[N, M]$ curve for all values of magnetization M. Higher-energy magnetization states are the subject of inherent interest and intense research. For example, the lowest energy triplet state plays a crucial role in phosphorescence [68,69], thermally activated delayed fluorescence [70,71] and singlet fission [72,73]. Within spin-DFT, such higher-energy magnetization states are accessible, as one may compute the lowest-energy state of each symmetry [74].

Theorem 1.—The $E_v[N_0, M]$ curve is piecewise linear with respect to magnetization M.

The structure of the $E_v(N_0, M)$ curve (where $N_0 \in \mathbb{N}$) can be elucidated by employing the technique, developed in W. Yang *et al.* [14], of constructing a system with external potential $v(\mathbf{r})$ that is composed of q copies of the same finite system with external potential $v_{\mathbf{R}_l}(\mathbf{r})$, with all copies being infinitely separated in space. The duplication of the system, at infinite separation, is a theoretical device used to consider its possible fractional charge and spin, without resorting to an ensemble treatment. The proof proceeds by analyzing the overall system of duplicates; however it is the individual finite subsystem (which may be strongly multireference in character) with which we are ultimately concerned. We have that

$$v(\mathbf{r}) = \sum_{l=1}^{q} v_{\mathbf{R}_l}(\mathbf{r}). \tag{7}$$

The total electron count is denoted by qN_0, where $N_0 \in \mathbb{N}$. It follows from the convexity condition that, at the infinite separation limit, N_0 electrons will localize on each of the q sites. For brevity, we will not repeat the electron count constraint $|M| \leq N_0 \in \mathbb{N}_0$, but note that it holds throughout Theorem 1 and Corollary 1.1. The total magnetization of the system is denoted by qM, where q and $qM \in \mathbb{Z}$. Typically, $M \notin \mathbb{Z}$ but $M \in \mathbb{Q}$ (which is supposed to be sufficiently dense in $\mathbb{R}$ for present purposes). The ground state of the system will be composed of p sites with a magnetization M_i, and $q-p$ sites with a magnetization M_j, where

$$qM = pM_i + (q-p)M_j, \quad p, q \in \mathbb{N}^0, \quad p \leq q, \quad M_i, M_j \in \mathbb{Z}, \text{ and } M_i \leq M \leq M_j. \tag{8}$$

For fixed values of the external parameters N_0 and M, the total number of sites q is chosen, together with the minimum M_i and maximum M_j, such that the total energy per site is minimized while satisfying the constraints of Eq. (8). Often one finds $M_i = M_j - 2$, but not always. For example, in the nitrogen atom $M_i = -3$ and $M_j = +3$ for $-3 < M < +3$. The choice of M_i and M_j is discussed further in SM, Sec. I.

One of the degenerate ground state wave functions of the system will consist of p sites with magnetization M_i and $q - p$ sites with magnetization M_j. As we describe in detail in SM, Sec. II, we may take the average of all such ground state wave functions, and analyze the associated spin-resolved site electron density. The piecewise linearity condition for magnetization, i.e.,

$$\begin{aligned} &E_v(N_0,M) = \omega E_v(N_0,M_i) + (1-\omega)E_v(N_0,M_j), \\ &M = \omega M_i + (1-\omega)M_j, \quad M_i, M_j \in \mathbb{Z} \ \& \ 0 \leq \omega \leq 1, \end{aligned} \tag{9}$$

thereby follows for all total energy functionals that are (a) exact for all v-representable spin densities, (b) size-consistent, and (c) translationally invariant.

We note that Gál and Geerlings [34] arrived at a similar piecewise linearity condition for magnetization by invoking a zero-temperature grand canonical ensemble.

Approximate total energy functionals E_v^{aprx} typically do not obey the piecewise linearity condition with respect to magnetization. We may refer to the intrinsic deviation of E_v^{aprx} from the piecewise linear $E_v(N_0, M)$ curve, between the (often inexact) energies at integer magnetization, as magnetic piecewise linearity error (MPLE),

$$\begin{aligned} E^{\mathrm{MPLE}}(N_0,M) = {}& E_v^{\mathrm{aprx}}(N_0,M) \\ & - [\omega E_v^{\mathrm{aprx}}(N_0,M_i) + (1-\omega)E_v^{\mathrm{aprx}}(N_0,M_j)]. \end{aligned} \tag{10}$$

Here, the electron count is a constant integer value N_0 and M, M_i, M_j and ω are given by Eq. (9). Figure 1 shows the $E^{\mathrm{MPLE}}(M)$ for the neutral helium atom.

MPLE differs from static correlation error (SCE) [15,83], which is defined as the spurious difference in total energy, due to the use of an approximate XC functional, between states that should be degenerate. MPLE instead is an error in the total energy of noninteger magnetization states, irrespective of whether such a state should be degenerate with one with integer magnetization. It would not be so, typically, in tilted-plane regions, or in a finite external magnetic field. Conversely, not all SCE can be described as MPLE, because SCE may refer to spurious energy differences between states of the same magnetization. An example of an SCE that is not an MPLE is the energy error that may arise in the description of the spherically symmetric boron atom [15].

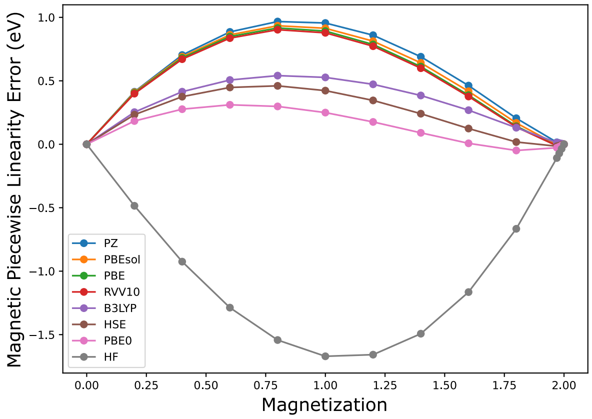

FIG. 1. The magnetic piecewise linearity error (MPLE) for the neutral helium atom exhibited by a variety of local [75], semilocal [5,76], hybrid [7–9,77], and van der Waals corrected [78] XC functionals, as well as Hartree-Fock (HF). As defined in Eq. (10), the MPLE for each approximate functional vanishes at certain integer values of spin magnetization. MLPE exhibits a substantial cubic component for all functionals shown. It approximately vanishes near full magnetization (but not elsewhere) for the hybrid functionals, reflecting the negative sign of MPLE for HF in this test system and hence cancellation of error [79]. Calculation details [80–82] can be found in SM, Sec. III.

Corollary 1.1.—The partial derivative of the $E_v[N_0, M]$ curve with respect to magnetization M is equal to half the difference between the spin-dependent frontier KS eigenvalues $\epsilon_{\mathrm{f}}^{\sigma}$, whenever the partial derivative exists,

$$\left(\frac{\partial E_v}{\partial M}\right)_N = \frac{1}{2}[\epsilon_{\mathrm{f}}^{\uparrow} - \epsilon_{\mathrm{f}}^{\downarrow}]. \tag{11}$$

A simple proof of this corollary is given in SM, Sec. IV (see also Refs. [24,28,34,84–87] therein), which avoids the need to invoke total single-particle energies or grand canonical ensembles.

Theorem 2.—The $E_v[N, M]$ surface obeys the tilted-plane condition described by Eq. (14).

Analysis of the $E_v[N_0, M]$ curve may be extended to include states with not only fractional magnetization M but also fractional electron count N. Again, one may construct an external potential given by Eq. (7). In this case typically both N and $M \notin \mathbb{Z}$, but the total system electron count and magnetization, qN and $qM \in \mathbb{Z}$. The ground state of this system will be composed of qc_i sites with electron count N_i and magnetization M_i, where i ranges from 1 to V_{count} with

$$\sum_{i=1}^{V_{\mathrm{count}}} c_i = 1, \quad 0 \leq c_i \leq 1, \quad N_i, M_i, qc_i \in \mathbb{Z}. \tag{12}$$

The values of c_i, N_i, and M_i are constrained so that

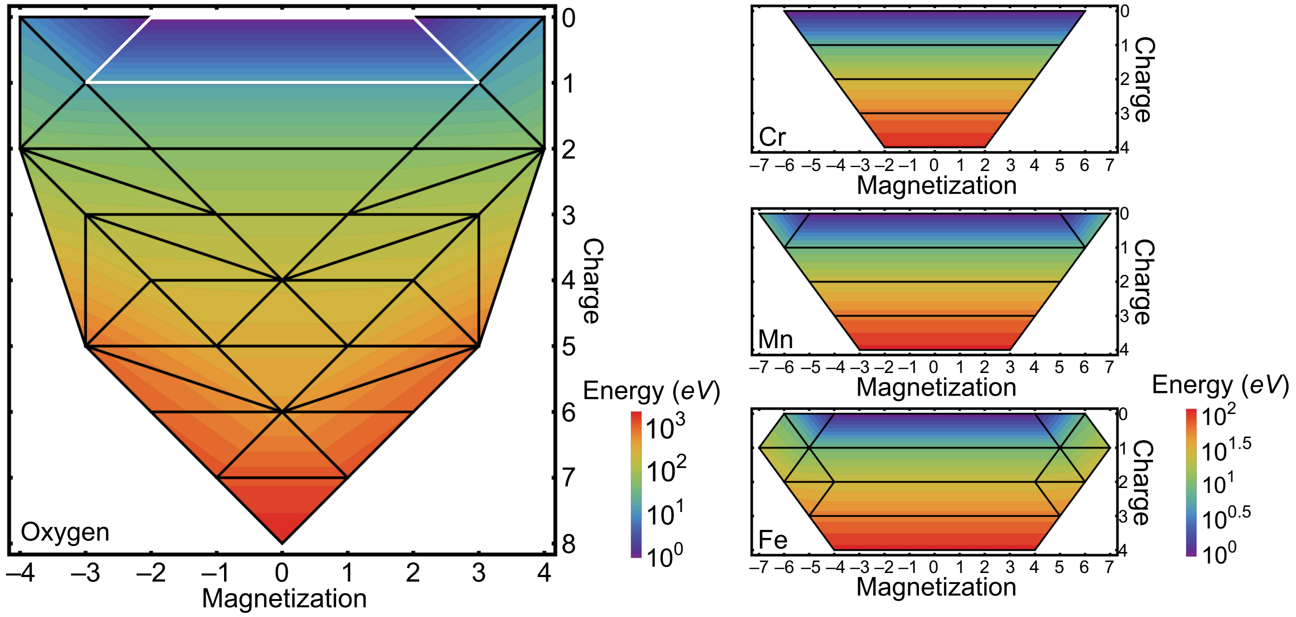

FIG. 2. The projection of the $E_v[N, M]$ surface of the oxygen, chromium, manganese, and iron atoms onto the N–M plane. The $E_v[N, M]$ curves are composed of a series of three- and four-sided planes with vertices at integer values of N and M. (The vertical axis is labeled in terms of the total atomic charge as opposed to total electron count.) The total energy varies linearly across each plane. Each plane is outlined in black. Energy contour lines are plotted at intervals of $10^{0.1x}$ eV. For each atom, the total energy values are based on available experimental National Institute of Standards and Technology reference data [88] and are given relative to the ground state total energy of the neutral atom in its lowest energy magnetization state, which is set to 1 eV for visualization purposes. Orbital and nuclear moments are not included. The $E_v[N, M]$ surface of the oxygen atom for charged states between +5 and +6 is composed of a series of five triangular shaped planes, four of which can neither be classed as a type 1 or a type 2 flat plane of X. Yang *et al.* [36]. Note that planes at the edges are omitted due to absence of experimental reference data. If any additional experimental reference data points not currently included are found to be low enough in energy, they could also affect the shape of the outlying, high-magnetization $E_v[N, M]$ surfaces shown here.

$$N = \sum_{i=1}^{V_{\text{count}}} c_i N_i \quad \text{and} \quad M = \sum_{i=1}^{V_{\text{count}}} c_i M_i. \tag{13}$$

Following an analogous derivation to that outlined in Theorem 1 (included in SM, Sec. I and Sec. II), one finds that, for $N, M \notin \mathbb{Z}$,

$$E_v[N, M] = \sum_{i=1}^{V_{\text{count}}} c_i E_v[N_i, M_i]. \tag{14}$$

Vertices in the energy landscape will occur at the specified integer values of electron count N_i and magnetization M_i. V_{count} is the number of vertices associated with a particular plane, typically equal to 3 or 4; however higher numbers of vertices are possible in very rare circumstances, as discussed in SM, Sec. V. To simplify discussion, we restrict $V_{\text{count}} = 4$; however, the method used to generate Fig. 2 includes no restriction on V_{count}.

In cases where the electron counts of the four states at the vertices satisfy $N_1 = N_2 = N_3 - 1 = N_4 - 1$ and the magnetizations $M_1 = -M_2$, $M_3 = -M_4$, with $E_v[N_i, M_i] = \min_M\{E_v[N_i, M]\}$, Eq. (14) simplifies to the flat-plane condition as outlined in Eq. (6). X. Yang *et al.* [36] and Cuevas-Saavedra *et al.* [37] report the existence of two types of flat-plane structures. These types are special cases (nonexhaustive ones; see Fig. 2 for an exception) of the more general condition outlined by Eq. (14), specifically when $c_4 = 0$. Generally, restricting c_4 to be zero prohibits the correct flat-plane structure of systems, e.g., the oxygen atom for $7 \leq N \leq 8$ and $|M| \leq 10 - N$, as highlighted in white in Fig. 2. The correct expression for this energy surface is detailed in SM, Sec. VI, along with further analysis of Fig. 2.

Gál and Geerlings [34] reported the existence of a tilted-plane energy surface but their energy expressions also have the $c_4 = 0$ restriction, meaning that (N_i, M_i) values in their energy expression will not always represent vertices in the energy landscape. The same is true for Chan's $E_v[N, M]$ energy expression [28]. To the best of our knowledge, a lifting of the $c_4 = 0$ restriction of the generalized flat-plane condition has only been discussed to date in the unpublished Ref. [35]. If we assume that (N_i, M_i) values represent vertices in the energy landscape, the $c_4 = 0$ restriction allows for triangular shaped planes but neglects planes of other shapes, such as isosceles trapezoids, which occur in the oxygen atom (Fig. 2).

A consequence worthy of future investigation is the appearance of derivative discontinuities both at noninteger values of total electron count N, and of spin-electron count $\frac{1}{2}(N \pm M)$, as seen, e.g., in the oxygen atom between charge states 5+ and 6+ with $1 \leq M \leq 2$ (Fig. 2). Knowledge of the occurrence of a tilted-plane energy surface has already been applied to correct the Perdew-Burke-Ernzerhof total energy of dissociated triplet H_5^+ in Ref. [46]. An analysis of the tilted-plane shape of the $E_v[N, M]$ surface for the He atom is shown in SM, Sec. III and the $E_v[N, M]$ surface for the multireference, quintuple bonded VCr, VMo, and CrMo heterodimers [89] are presented in SM, Sec. VII. Sample degeneracy-dependent tilted-plane structures for an isolated d-orbital subspace are shown in SM, Sec. VIII.

In conclusion, the piecewise linearity condition with respect to magnetization and the tilted-plane condition were derived from first principles using the infinite-separation-limit technique, and the magnetic analog of the DFT Koopmans' theorem was derived from the chain rule. These exact conditions have been derived for all formulations of DFT that are exact for all v-representable spin densities, size-consistent, and translationally invariant. It is important to note that these exact conditions apply only to the lowest $E_v[N, M]$ energy surface. By performing a constrained search over states of a specified spin multiplicity [74], it is possible to access other quantum states within DFT that are not located on this energy surface, for example, the lowest-energy singlet state of a system with a triplet ground state.

We have found that many standard density functional approximations violate these exact conditions. These three exact quantum mechanical conditions may aid in the development of post-DFT methods and functional approximations, machine learning, and alchemical approaches in both condensed matter physics and quantum chemistry, and error-correction techniques involving total energies in quantum science. We find that in order to approach the exact limit, energy functionals of occupancies must necessarily take different forms depending on symmetry-imposed degeneracies.

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