A bivariate potential-density view of Kohn-Sham iteration

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A bivariate perspective on density functional theory is proposed, privileging neither potential nor density a priori. For a minimal abstract formulation of Kohn-Sham iteration, suitable for wide application, this view leads to the following conclusions. (i) Exact solutions to approximate problems are as natural a notion as approximate solutions to exact problems. (ii) The standard variety of iterative strategy finds little support. (iii) An alternative strategy can be shown to usually make progress (with slight breach of the abstraction barrier). (iv) Given the density/potential pair at a calculational stage, the natural goodness-of-approximation measure — excess of interacting energy over the target ground state energy — is not computationally feasible, but can be bounded in terms of the feasible potential distance between the current exact problem and the target problem.

1. INTRODUCTION

Over the past five decades, ground-state density functional theory (DFT) has developed to become a ubiquitous tool in physics, chemistry, materials science, and beyond, particularly in the dominant Kohn-Sham (KS) form. The KS formulation is distinguished first by a splitting of the intrinsic energy into that of non-interacting electrons plus the Hartree-exchange-correlation energy, but also by a distinctive variety of iterative procedure. Although Kohn-Sham iteration generally works well in practice, why such a method even makes progress — the motivating question for this investigation — seems little explored.

Kohn-Sham iteration is traditionally understood to unfold in density space: a cycle begins with a density and returns a new (presumably better) one, the process continuing until some cycle-to-cycle change is deemed suitably small. I intend to alternative bivariate view of Kohn-Sham theory that privileges neither density nor potential a priori; potential becomes an independent variable just like density. From this perspective, the history of any iterative calculation is a sequence of potential/density ground pairs for both noninteracting and interacting problems (slogan: approximate problems rather than approximate solutions). A natural potential-driven family of feasible strategies emerges as significantly better-motivated than the standard density-centric family. That claim is supported by a demonstration that, for concrete models, the strategy \( \text{Str}^{\text{min}} \) can usually be expected to make progress (Prop. 2) in the sense that total energy over the target ground state energy (the natural goodness-of-approximation measure) decreases. While the absolute value of that measure is not computationally feasible, Prop. 3 shows it can be bounded by the computationally feasible distance in potential between the current exact problem and the target problem.

An abstract axiomatic approach is taken here. (Laestadius et al. have recently proposed a similar treatment, based on a Moreau-Yosida regularization of DFT, but with somewhat different aims.) The high-level structure of a Kohn-Sham calculation is independent of quantum mechanics, and the important question is what can be implemented at acceptable computational effort, not implementation details (i.e., how). Abstraction highlights this and guards against surreptitious injection of things we think we know. The resulting formulation embraces ordinary Kohn-Sham DFT in continuous and discrete (e.g., tight-binding) versions, Hartree self-consistent field calculations, and appropriate forms of nonzero-temperature quantum DFT and classical density functional theory, as well as, perhaps, other calculational frameworks whose kinship will be more easily recognized through the abstraction.

2. PRÉCIS OF GENERAL DFT IN CONVEX ANALYSIS FORM.

The quantum mechanical problem addressed by DFT is that of finding the ground state energy and electronic density for a system of \( N \) interacting electrons subject to a specified external one-body potential. Denote kinetic and kinetic-plus-interaction energy of an \( N \)-electron pure state by

\[
F_0(\psi) = \langle \psi | T | \psi \rangle, \quad F(\psi) = F_0(\psi) + \langle \psi | V_{\text{int}} | \psi \rangle, \quad \tag{1}
\]

and the associated particle density by

\[
dens \psi(x) = N \sum_x \int |\psi(x_1, x_2, \ldots, x_N)|^2 \, dx_2 \cdots dx_N.
\]

These have natural linear extensions to functions on the set \( \text{State} \) of mixed states: with \( \gamma = \sum_i \lambda_i |\psi_i\rangle \langle \psi_i| \), \( F_0(\gamma) = \sum_i \lambda_i F_0(\psi_i) \), etc. The intrinsic energy of a density is the minimum of the intrinsic energy over all states with that density:

\[
F(\rho) = \inf \{ F(\gamma) : \gamma \in \text{State}, \, \text{dens} \gamma = \rho \}. \quad \tag{2}
\]
With the notation
\[ \langle v, \rho \rangle := \int v(x) \rho(x) \, dx, \] (3)
the minimal energy attainable with density \( \rho \) in the presence of an external potential \( v \) is \( F(\rho) + \langle v, \rho \rangle \), so the ground energy functional is
\[ E(\rho) = \inf_{\rho} \{ F(\rho) + \langle v, \rho \rangle \}. \] (4)

\( E \) is a slight modification (by signs) of the convex conjugate, or Fenchel transform\(^{[14,17]}\) of \( F \).

For an unambiguous formulation, we need to specify spaces \( B \) of densities and \( B' \) of potentials. Lieb\(^{[12]}\) took \( B = L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \) and \( B' = L^\infty(\mathbb{R}^3) + L^{3/2}(\mathbb{R}^3) \). All we require though, is that \( B \) be a Banach space and \( B' \) its dual space. The minimization in (4) should thus be carried out over \( B \). Now, since \( F \) is convex and lower semicontinuous,
\[ F(\rho) = \sup_{\nu \in \nu} \{ E(\nu) - \langle v, \rho \rangle \}. \] (5)

The subdifferential at \( x \in B \) of a convex function \( f \) is the subset of \( B' \) defined by
\[ \xi \in \partial f(x) \iff \forall y, f(y) \geq f(x) + \langle \xi, y - x \rangle. \] (6)
\( \xi \in \partial f(x) \) is called a subgradient at \( x \). The hyperplane specified by \( \xi \) and touching the graph of \( f \) at \( (x, f(x)) \) is nowhere above the graph, so a subgradient has the fundamental geometric significance of a derivative and can often stand in when no classical derivative exists. For concave \( f \), the superdifferential \( \partial^f \) is just the subdifferential of \( -f \), and if \( f \) is defined on \( B' \) (e.g., \( E \)), the sub- or superdifferential is as in (6) with \( B \) and \( B' \) interchanged.

Readers who find this technical machinery disorienting are advised to simply read all sub- or superdifferentials as ordinary derivatives; the core message survives.

3. KOHN-SHAM THEORY AND FEASIBILITY

Unfortunately, the general framework just sketched provides no methods to actually calculate \( E(\nu) \) or ground densities. The fundamental idea of Kohn-Sham theory is to split \( F \) as
\[ F = F_0 + \Phi \] (7)
where \( F_0(\rho) = \inf \{ \mathcal{F}_0(\gamma) : \gamma \in \text{State}, \text{dens} \gamma = \rho \} \) is the non-interacting version of \( F \), often denoted \( T \). \( \Phi \) (Hartree-exchange-correlation energy) is then defined by (7) as whatever is required to make up the difference. The form of iterative schemes is limited by which of the functions/functionals involved can be practically computed. A the notion of ‘feasibility’ is therefore central. Informally, a function \( f : A \rightarrow B \) is feasible if, given an argument \( x \in A \), \( f(x) \) is computable at acceptable cost. Here is a loose axiomatization. Identity operations and compositions of feasible operations, elementary operations such as arithmetic, tupling, component projection and evaluation by case are all feasible. Unbounded search (while loops) can be feasible, if guaranteed to return. For normed vector spaces \( (B, B') \), vector addition, scalar multiplication, the norms \( || \cdot || \), and vector/dual-vector pairing \( (\cdot, \cdot) \) are feasible. The critical question is, what are the KS-specific basic feasible operations? These are \( E_0, \overline{\partial}E_0 \) (noninteracting ground energy and density), \( \Phi \) and \( D\Phi \) (Hartree-exchange-correlation energy and density, respectively). \( D \) here denotes an ordinary (say, Gâteaux) functional derivative. Things not on this list are \( F_0, \partial F_0, F, \partial F, E \) and \( \overline{\partial}E \). The last two are essentially the object of a KS calculation, and that they are not basic feasible operations is the reason indirect iterative methods are used to approximate them.

4. ABSTRACT KOHN-SHAM MODELS

We now define abstract Kohn-Sham models by the following axioms.

(Ref) Reference system:
\[ F_0 : B \rightarrow \mathbb{R} \cup \{\infty\} \] (8)
is a proper (not everywhere infinite) convex lower semicontinuous function on the Banach space \( B \), with an up-to-signs Fenchel conjugate \( E_0 : B' \rightarrow \mathbb{R} \cup \{-\infty\} \) [Eq. (3)] which is everywhere finite. (Concavity and upper semicontinuity are automatic.)

(Pert) Perturbation:
\[ \Phi : B \rightarrow \mathbb{R} \] (9)
is Gâteaux differentiable.
\[ F = F_0 + \Phi : B \rightarrow \mathbb{R} \cup \{\infty\} \] (10)
and its partner \( E \) have the same attributes specified for the reference system.

The subdifferential of \( F \) therefore decomposes as (double arrow denotes set-valued function)
\[ \partial F = \partial F_0 + D\Phi : B \rightrightarrows B'. \] (11)
As a consequence, at any \( v \in B' \), either both \( F_0 \) and \( F \) are subdifferentiable, or neither is. \( F_0 \) and \( \Phi \) define the perturbed system: approximations that may be embodied by \( \Phi \) are not our concern.

(Feas) Feasibility: \( E_0, \overline{\partial}E_0 \), \( \Phi \) and \( D\Phi \) are feasible.
Here, \( \overline{\partial}E_0 \) denotes an implementation of \( \overline{\partial}E_0 \) which is required only to return a single supergradient, or inform us if none exists. (Feas) does not state that anything is
infeasible, and computational advances might well induce us to expand the list of feasible operations.

The preceding assumptions are always considered to be in force. *(Feas)* is not used in anything labelled ‘Lemma’ or ‘Proposition’ but is critical to the interpretive gloss. Eventually, we will need to consider the following supplementary global regularity assumptions.

\[(HXC) \; \partial E : B \to B' \text{ is (norm–norm) continuous.}\]

\[(Lip) \; E \text{ is Lipschitz continuous.}\]

Our attitude toward \(\Phi\), as with everything else, intends to take computational praxis into account. Generally, it is given by an explicit formula and is therefore rather nice. An arbitrarily tiny smoothing, if required to satisfy either *(Pert)* or *(HXC)*, would probably not impair the quality of approximation to the exact functional.

5. WALKING AMONG THE GROUND PAIRS

Making the bivariate perspective manifest, we roll \(F\) and \(E\) together into the excess energy

\[\Gamma(v, \rho) := F(\rho) + \langle v, \rho \rangle - E(v).\]  \[(12)\]

\(\Gamma(v, \rho)\) is how close states of density \(\rho\) can get to the ground energy, in presence of \(v\). Working with \(\Gamma\) satisfies the desire to treat densities and potentials on equitable footing, not alternately, as with \(F\) and \(E\), but simultaneously. By definition of \(E\), \(\Gamma \geq 0\), and if \(\Gamma(v, \rho) = 0\), then \((v, \rho)\) comprises a ground pair, the entire set of which is denoted

\[\text{GP} := \{(v, \rho) \in B' \times B \mid \Gamma(v, \rho) = 0\}.\]  \[(13)\]

Similarly, \(\Gamma_0\) and \(\text{GP}_0\) belong to the reference system. \(\text{GP}\) can be characterized in terms of the subdifferential \(\partial F(\rho)\) of \(F\) or the superdifferential \(\overline{\partial E}(v)\) of \(E\), as

\[(v, \rho) \in \text{GP} \iff -v \in \partial F(\rho) \iff \rho \in \overline{\partial E}(v).\]  \[(14)\]

\(\Gamma\) is a convex function of \(\rho\) at fixed \(v\), and of \(v\) at fixed \(\rho\). Partial subdifferentials, relative to the subscripted variable, are

\[\partial_\rho \Gamma(v, \rho) = \partial F(\rho) + v\]  \[(15a)\]

\[\partial_v \Gamma(v, \rho) = \rho - \overline{\partial E}(v).\]  \[(15b)\]

What do we want to do?

**Problem A:** given \(v^\circ \in B'\), find \((v^\circ, \rho^\circ)\) in \(\text{GP}\), or a near enough approximation thereof.

The superscript ‘\(\circ\)’ here is supposed to look like a bullseye, as it indicates a target. Options for what ‘approximation’ means will emerge in time.

Our stock of basic feasible operations severely constrains the ways Problem A can be approached. According to *(Feas)*, the partial function

\[G := v \mapsto (v, [\overline{\partial E}_0(v)]) : B' \xrightarrow{\text{feas}} \text{GP}_0\]  \[(16)\]

is feasible (hence ‘feas’ above the partial function arrow). \(G\) generates a point in \(\text{GP}_0\) or informs us that none exists with first coordinate \(v^\circ\). From potential \(v\) are obtained the reference and perturbed ground pairs \(Gv = (v, \overline{\partial E}_0(v)) = (v, \rho)\) and \(\hat{G}(v) = (\hat{v}, \rho)\). The plain-vanilla strategy \(\text{Str}_1\) says to try a new potential \(v + \Delta v\).

![FIG. 1. Highly schematic illustration of the bivariate perspective.](image)

In conventional DFT language, the explanation of this is that if \(\rho\) is a non-interacting ground density for potential \(v\), then it is an interacting ground density for \(v\) minus the Hartree-exchange-correlation potential of \(\rho\). In our abstract setup, we argue that since \(\rho \in [\overline{\partial E}_0(v)]\) iff \(v \in [\partial F_0(\rho)]\), \[(11)\] implies that \(v + D\Phi(\rho) \in [\partial F(\rho)]\). Composing with \(G\) gives us a map from potentials to interacting ground pairs:

\[\hat{G} := \wedge \circ G : B' \xrightarrow{\text{feas}} \text{GP}.\]  \[(18)\]

\(\wedge\) is not really anything new, but the bivariate perspective, vividly illustrated in Fig.\[(11)\] brings an increased clarity.
For convenience, we introduce a ‘hat’ operation
\[ \hat{\nu} := \pi_2 \circ G (v) = v + D\Phi \circ \overline{\partial E_0} (v), \] (19)
on potentials, so that if \( Gv = (v, \rho) \), then \( \hat{G}v = (\hat{v}, \rho) \).

Given \((\hat{v}, \rho) \in \text{GP}_0\), can we say something about how ‘close’ it is to a solution of Problem \( \Lambda \)? The \textit{deficit}
\[ \hat{E}v := v^\circ - \hat{v} \] (20)
of \( \hat{v} \) offers one answer to that question. Suppose, now, two points \((v, \rho) \) and \((v', \rho') \) in \( \text{GP}_0 \). \( \Gamma(v^\circ, \rho) \) is not evidently feasible, since \( E_0(v^\circ) \) is unknown, but the difference
\[ P := (v', \rho'), (v, \rho) \mapsto \Gamma(v^\circ, \rho') - \Gamma(v^\circ, \rho) \] (21)
is so. It tells which of \( \rho \) or \( \rho' \) is energetically closer to a ground state of \( v^\circ \), and by how much. Feasibility of \( P \) follows that of
\[ F_{\text{GP}_0} := (v, \rho) \mapsto F(\rho) : \text{GP}_0 \rightarrow \text{Feas} \rightarrow \mathbb{R}, \] (22)
which, in turn, follows from feasibility of \( E_0 \) and \( \Phi \). \( F_{\text{GP}_0} \) is essentially the original definition offered by Hohenberg and Kohn\[1\] for the intrinsic energy.

Although the starter kit of feasible operations in \( \text{Feas} \) is stronger than \( G, \hat{\Delta} \) and \( P \), there is at least a hint here that the latter set captures all the operations which are useful in solving Problem \( \Lambda \).

6. STRATEGIES

Now we consider how to select potentials to feed to \( G \). Such a choice must be informed by the preceding history of input-output \((v_m, \hat{G}v_m)\) pairs
\[ \text{hist}_n = (v_1, \hat{G}v_1), (v_2, \hat{G}v_2), \ldots, (v_n, \hat{G}v_n) \] (23)
and requires a \textit{strategy}. The “plain vanilla” strategy is
\[ \text{Str}^\text{std}_1(v^\circ, \text{hist}_n) = v^\circ - D\Phi(\rho_n) \]
\[ = v_n + (v^\circ - \hat{v}_n) \]
\[ = v_n + \hat{\Delta}v_n. \] (24)
A rough gloss is that \( \text{Str}_1 \) embodies the hypothesis that \( \hat{v} - v \) varies little with \( v \), and uses the last stage of \( \hat{\Delta} \) to calculate it.

Alas, \( \text{Str}_1 \) has a well-known tendency toward “charge sloshing” instability. “Mixing”, though, is an effective cure. For example,
\[ \text{Str}^\lambda_1 = \lambda \text{Str}^\text{std}_1 + (1 - \lambda) \text{Str}_0, \quad 0 < \lambda < 1, \] (25)
is a convex mixing of \( \text{Str}^\text{std}_1 \) with the extremely stable \textit{repeat} strategy
\[ \text{Str}_0(v^\circ, \text{hist}_n) = v_n. \] (26)
The strategy \( \text{Str}^\lambda_1 \) follows the advice of \( \text{Str}^\text{std}_1 \), but cautiously, taking only a small step in the suggested direction.

Standard practice does not, however, follow \( \text{Str}^\text{std}_1 \). In order to describe the standard strategy, we need an augmented kind of history,
\[ \text{hist}^+_n := (\rho^\text{in}_1, v_1; \hat{v}_1, \rho_1), \ldots, (\rho^\text{in}_n, v_n; \hat{v}_n, \rho_n). \] (27)
Here, \( \rho^\text{in} \), with no direct physical interpretation, serves to \textit{parametrize} \( v_k \) according to
\[ v_k := v^\circ - D\Phi(\rho^\text{in}_k). \] (28)
The standard mixing strategy describes \( v_{n+1} \) indirectly, through its parametrization \( \rho^\text{in}_{n+1} \), with \( \text{hist}^+_n \) as input:
\[ \text{Str}_\lambda^\text{std} : \rho^\text{in}_{n+1} = \lambda \rho_n + (1 - \lambda) \rho^\text{in}_n, \quad 0 < \lambda \leq 1. \] (29)
It is easily verified that \( \text{Str}_\lambda^\text{std} = \text{Str}_1 \). What is somewhat more surprising is that \( \text{Str}^\lambda_1 \) can be essentially implemented through unaugmented histories according to
\[ \text{Str}^\lambda_1(v^\circ, \text{hist}) \approx v^\circ - D\Phi \left( \lambda \sum_{k=0}^{\infty} (1 - \lambda)^k \rho_{n-k} \right), \] (30)
where \( \rho_k = \rho_0 \) for \( k < 0 \). That is, starting with a long run of \( \text{Str}^\text{std}_1 \), there is very little difference between continuing to follow that strategy or switching to the one on the right-hand side of \( \text{(36)} \).

There is no particular reason why \( \lambda \) should have to be the same for every cycle, however. Allowing it to vary gives us the families of strategies \( \text{Str}^\nu \) and \( \text{Str}^{\lambda\text{std}}_\lambda \). From the bivariate perspective, the standard strategies are more difficult to describe than the \( \text{Str}^\nu \), because they involve a layer of indirection, the purpose of which is opaque. However, none of the strategies discussed is well-motivated at this point. Correcting that is a main concern henceforth. We will find some justification for \( \text{Str}^\nu \), but none for \( \text{Str}^{\lambda\text{std}} \).

7. PROGRESS

Recalling \( \text{(21)} \), we say that an abstract KS strategy \textit{makes progress} if it delivers a sequence \( \rho_n \) such that \( \Gamma(v^\circ, \rho_n) \) is decreasing. In that case, the sequence \( (\Gamma(v^\circ, \rho_n))_n \) converges, but not necessarily to zero. A strategy may hand us a potential \( v \) such that \( \overline{\partial E_0}(v) \) is empty, in which case there is no way to proceed. Additional strong hypotheses (e.g., \( F_0 \) bounded below, \( B \) reflexive) could stamp out this problem. However, we are content to accept such feasibly recognizable exceptional situations, since the aim is an understanding of why progress may \textit{usually} be possible.

A. First try

A first attempt at a progress theorem is the same in essence as one previously obtained by Wagner \textit{et al.}\[18\],
which was recently corrected and put into a rigorous form by Laestadius et al. [8].

Proposition 1. If \( (v, \rho), (v + \Delta v, \hat{\rho}) \in \mathbb{G} \) and \( \Delta v \neq 0 \), then
\[
\frac{d}{d\lambda} \Gamma(v^\circ, (1 - \lambda)\rho + \lambda\hat{\rho}) \bigg|_{\lambda=0} < 0,
\]
(31)
whenever the derivative exists.

The following generalization of a monotonicity inequality \([8, 17, 19]\), previously derived in a DFT context \([18, 20]\) plays a role in the proof of Prop. 1 and may be of independent interest.

Lemma 1 (Cross-difference identity).
\[
\Gamma(v, \rho) + \Gamma(v', \rho') - \Gamma(v, \rho') - \Gamma(v', \rho) = \langle v - v', \rho - \rho' \rangle.
\]
(32)

Proof. Each of \( v, v', \rho, \) and \( \rho' \) appears on the left-hand side of (32) as an argument of two \( \Gamma \)'s, one with a minus sign. Thus, all the \( \Gamma \)'s and \( E \)'s cancel out. Tallying up the potential-density pairings gives the right-hand side. \( \Box \)

Mostly, we use Lemma 1 in the form of the monotonicity inequality
\[
(v, \rho), (v', \rho') \in \mathbb{G} \Rightarrow \langle v - v', \rho - \rho' \rangle = -\Gamma(v', \rho) - \Gamma(v', \rho') \leq 0.
\]
(33)
Note that, if either \( (v', \rho) \) or \( (v, \rho') \) fails to be a ground pair, then the inequality is strict.

Proof of Prop. 1. Apply monotonicity of \( \Gamma_0 \) to the two points \( (v, \rho), (v + \Delta v, \hat{\rho}) \in \mathbb{G} \) (as illustrated in Fig. 1 of the main text) to obtain
\[
\langle \hat{\rho} - \rho, \Delta v \rangle < 0.
\]
(34)
The inequality is strict because \( (v + \Delta v, \rho) \notin \mathbb{G} \). For, if both \( (v, \rho) \) and \( (v + \Delta v, \rho) \) are in \( \mathbb{G} \), it follows that \( (v^\circ, \rho) \notin \mathbb{G} \), contrary to assumption.

According to [15a],
\[
\Delta v = -(v^\circ - \Delta v) + v^\circ \in \partial_\rho \Gamma(v^\circ, \rho),
\]
so that by (34), \( \langle \hat{\rho} - \rho, \partial_\rho \Gamma(v^\circ, \rho) \rangle \) contains a negative number. Finally, the differentiability assumption of the theorem implies that
\[
\langle \hat{\rho} - \rho, w \rangle = \frac{d}{d\lambda} \Gamma(v^\circ, \rho + \lambda[\hat{\rho} - \rho]) \bigg|_{\lambda=0}
\]
(35)
for every \( w \in \partial_\rho \Gamma(v^\circ, \rho) \), so the conclusion follows. \( \Box \)

While the inequality (31) is suggestive and encouraging, it is unclear how the implied strategy could be feasibly implemented. It asks us to obtain points on \( \mathbb{G} \) with density components linearly interpolating between \( \rho \) and \( \hat{\rho} \). The discussion of walking among the ground pairs shows that we need to know what potentials will produce those densities, and the Proposition offers no guidance for that. We must try a different route.

B. Progress redux

In the interest of notational simplicity, subscripts on \( \rho \) and \( v \) are repurposed in the following discussion. We suppose that a potential \( v \) is in hand, and consider how progress can be made in the next cycle, without reference to previous steps. So, with \( v_0 = v \) and \( v_1 = v_0 + \Delta v_0 \), define \( v_\lambda := (1 - \lambda)v_0 + \lambda v_1 \) for \( 0 \leq \lambda \leq 1 \) by linear interpolation, and then \( \rho_\lambda \) via \( G : (v_\lambda, \rho_\lambda) = Gv_\lambda \). In contrast to densities suggested by Prop. 1, \( \rho_\lambda \) here is perfectly feasible since \( v_1 \) is so. Of course, we have to assume that \( \rho_0 \) and \( \rho_1 \) exist. The question now is whether \( \Gamma(v^\circ, \rho_\lambda) - \Gamma(v^\circ, \rho_0) < 0 \) for some \( \lambda > 0 \). The following Lemma exposes some sufficient conditions.

Lemma 2 (Progress). With the preceding notation,
\[
\left[ \Gamma(v^\circ, \rho_\lambda) - \Gamma(v^\circ, \rho_0) \right] + \Gamma(v_\lambda, \rho_0)
\]
can be expressed in either of the following two ways:
\[
\lambda^{-1} \langle v_\lambda - v_0, \rho_\lambda - \rho_0 \rangle - \langle \hat{v}_\lambda - \hat{v}_0, \rho_\lambda - \rho_0 \rangle, \tag{36}
\]
\[
(1 - \lambda) \langle \Delta v_0, \rho_\lambda - \rho_0 \rangle + \langle D\Phi(\rho_0) - D\Phi(\rho_\lambda), \rho_\lambda - \rho_0 \rangle. \tag{37}
\]
In either form, the first term is negative. An alternative expression for the first term of (37) is given by
\[
\langle \Delta v_0, \rho_\lambda - \rho_0 \rangle = -\frac{1}{\lambda} \left[ \Gamma_0(v_\lambda, \rho_0) + \Gamma_0(v_0, \rho_\lambda) \right]. \tag{38}
\]

Proof. The definition (12) of excess energy gives
\[
(v, \rho) \in \mathbb{G} \Rightarrow \Gamma(v', \rho) = F(\rho) + \langle v', \rho \rangle - E(v') \tag{39}
\]
\[
= E(v) - E(v') + \langle v' - v, \rho \rangle.
\]
Apply this identity three times, with \( v, \rho, v' = \hat{v}_\lambda, \rho_\lambda, v^\circ \), with \( v, \rho, v' = \hat{v}_0, \rho_0, v^\circ \), and with \( v, \rho, v' = \hat{v}_0, \rho_0, \hat{v}_\lambda \). Combining the right-hand sides with appropriate signs, all \( E \) terms cancel in pairs, yielding
\[
\Gamma(v^\circ, \rho_\lambda) - \Gamma(v^\circ, \rho_0) + \Gamma(v_\lambda, \rho_0) = \langle v^\circ - \hat{v}_\lambda, \rho_\lambda - \rho_0 \rangle \tag{40}
\]
Substitute
\[
\langle v^\circ - \hat{v}_0 + \Delta v_0, \hat{v}_0 + v_1 - v_0 \rangle
\]
to the right-hand side of (40) to obtain
\[
\Gamma(v^\circ, \rho_\lambda) - \Gamma(v^\circ, \rho_0) + \Gamma(v_\lambda, \rho_0) = \langle v_0 - v_1, \rho_\lambda - \rho_0 \rangle - \langle \hat{v}_\lambda - \hat{v}_0, \rho_\lambda - \rho_0 \rangle.
\]
This is (36).
To get (37) from that, substitute \( \hat{v}_\lambda - \hat{v}_0 = v_\lambda - v_0 + D\Phi(\rho_0) - D\Phi(\rho_\lambda) \). The alternate form (38) is obtained by application of the cross-difference identity, Lemma 1. \( \Box \)
The general shape of how Lemma 2 should be used is clear. Will $\lambda \left| \langle D\Phi (\rho_0) - D\Phi (\rho_\lambda) \rangle, \rho_\lambda - \rho_0 \rangle \right| \leq \Gamma_0(v_\lambda, \rho_\lambda) + \Gamma_0(v_0, \rho_0)$ (equivalently $\left| \langle v_\lambda - v_0, \rho_\lambda - \rho_0 \rangle \right|$), say for small $\lambda$? Controlling the hopefully-small quantity requires some constraint on $D\Phi$. Therefore, we now enforce the regularity assumption (HXC) that $D\Phi$ is norm-norm-continuous. Then,

$$\left| \langle D\Phi (\rho_0) - D\Phi (\rho_\lambda), \rho_\lambda - \rho_0 \rangle \right| = o \left( \| \rho_\lambda - \rho_0 \| \right).$$

(41)

In that case, progress would be assured if $\| \rho_\lambda - \rho_0 \| \to 0$ as $\lambda \to 0$ and either side of (38) was bigger than $o \left( \| \rho_\lambda - \rho_0 \| \right)$, requirements which refer only to the reference system.

**Lemma 3.** Assuming (HXC), $\Gamma (v^\circ, \rho_\lambda) - \Gamma (v^\circ, \rho_0) < 0$ for sufficiently small $\lambda > 0$, if

$$\| \rho_\lambda - \rho_0 \| \to 0 \text{ as } \lambda \to 0,$$

and

$$\liminf_{\lambda \to 0} \left( \frac{\left| \langle v_\lambda - v_0, \rho_\lambda - \rho_0 \rangle \right|}{\| v_\lambda - v_0 \| \| \rho_\lambda - \rho_0 \|} \right) > 0.$$

(43)

If $\| v_\lambda - v_0 \| \to 0$ as $\lambda \to 0$, then $\Gamma (v^\circ, \rho_\lambda) - \Gamma (v^\circ, \rho_0) < 0$ for some $c > 0$.

**Remark 7.1.** As stated, the Lemma implies that $\overline{\partial E_0(v_\lambda)} \neq \emptyset$ for all $0 \leq \lambda < 1$. A minor modification which requires only $\overline{\partial E_0(v_{\lambda_0})} \neq \emptyset$ for a sequence $\lambda_n$ strictly decreasing to zero is also valid.

**Proof.** (38) is clearly equivalent to

$$\left| \langle \hat{\Delta} v_0, \rho_\lambda - \rho_0 \rangle \right| > c \| \rho_\lambda - \rho_0 \|$$

(45)

follows by application of (38). By appeal to (41) and (37) from Lemma 2 $\Gamma (v^\circ, \rho_\lambda) - \Gamma (v^\circ, \rho_0) < 0$. $\square$

It is unclear what sort of non-draconian abstract conditions would ensure the behavior described in Lemma 3 so we consider now concrete quantum-mechanical models. There, the desired result is predicted by ordinary nondegenerate perturbation theory, validity of which is ensured by the hypotheses of Prop. 2. Note that a potential in $L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ is Kato-tiny with respect to kinetic energy.

**Proposition 2.** Assume a concrete $L^1 \cap L^3$ quantum mechanical ground state KS model obeying (HXC). Then, if $v^\circ$, $v_0$ and $\Delta v_0$ are Kato-tiny relative to kinetic energy and $\rho_0$ is the density of an isolated nondegenerate eigenvalue, $\Gamma (v^\circ, \rho_\lambda) - \Gamma (v^\circ, \rho_0) < 0$ for sufficiently small $\lambda > 0$. If $D\Phi$ is always Kato-tiny along with $v^\circ$ and the initial $v_0$, then the Kato-timiness condition is preserved by any $\text{Str}^2$ strategy.

The proof is somewhat technical and will not be required for anything else.

**Proof.** Since $v_\lambda = v_0 + \lambda \hat{\Delta} v$, we are dealing with a perturbation problem with perturbation parameter $\lambda$ and the idea is to (i) impose conditions so that naive nondegenerate perturbation theory for the ground state is on a solid basis and (ii) see that the naive predictions are good enough.

As for (i), the restrictions on potentials ensure a type-A family [21] of Hamiltonians $H_\lambda$ all with a common domain, equal to that of the kinetic energy, namely the Sobolev space $H^2(\mathbb{R}^{3N})$. Recall that, for unbounded operators $A$ and $B$ on a Hilbert space, $B$ is relatively $A$ bounded if the domain of $B$ is contained in that of $A$ and there are $\epsilon$ and $c(\epsilon)$ such that

$$\| B\psi \| \leq \epsilon \| A\psi \| + c(\epsilon) \| \psi \|$$

(46)

for all $\psi$ in the domain of $B$. $B$ is Kato-tiny (see A.14 of Ref. [24] if $\epsilon$ can be taken as small as desired. The requirement of an isolated nondegenerate ground state then guarantees perturbation theory for $E_0(v_\lambda)$ and corresponding ground state vector $\psi_\lambda$ which is analytic in $\lambda$ on some neighborhood of zero.

Turning to (ii), according to (41) in Lemma 3, it suffices to show that $\| \rho_\lambda - \rho_0 \| < c(\epsilon)$ and $\Gamma_0(v_\lambda, \rho_0), c(\epsilon)$, for strictly positive constants $c', c''$. Naive perturbation theory gives those inequalities, although that for the density is a little tricky since with the requirement of an isolated nondegenerate ground state is on a solid basis and (ii) see that the naive predictions are good enough.

Applying the Cauchy-Bunyakovski-Schwartz (CBS) inequality,

$$\| \rho_\lambda(x) - \rho_0(x) \| \leq \left( \int dx_2 \cdots dx_N \left( |\psi_\lambda|^2 - |\psi_0|^2 \right) \right)^{1/2} \leq 2 \rho_0(x)^{1/2} \eta_\lambda(x)^{1/2} + \eta_\lambda(x),$$

(47)

where

$$\eta_\lambda(x) := \int dx_2 \cdots dx_N |\psi_\lambda - \psi_0|^2.$$  

(48)

Now using the elementary inequality $(a + b)^3 \leq 8a^3 + 8b^3$ for $a, b > 0$, and integrating over $x$, 

$$\int |\rho_\lambda(x) - \rho_0(x)|^2 dx \leq 16 \int \rho_0^{3/2} \eta_\lambda^{3/2} dx + 2 \int \eta_\lambda^3 dx \leq 16 \rho_0^{3/2} \| \eta_\lambda \|^{3/2} + 2 \| \eta_\lambda \|^3.$$  

(49)

We will therefore have succeeded in our task if we merely show that

$$\| \eta_\lambda \| \to 0, \text{ as } \lambda \to 0.$$  

(50)

To that end, we now apply a Sobolev inequality to obtain

$$\| \eta_\lambda \|^3 \leq c \int |\nabla \sqrt{\eta_\lambda^2} |.$$  

(51)
for some positive constant $c$. Another application of the CBS inequality and the definition of $\eta$ yields

$$\nabla \sqrt{\eta} = \frac{1}{2} \sqrt{\eta} \int dx_2 \cdots dx_N 2 \text{Re} \left( (\psi_\lambda - \psi_0)^* \nabla (\psi_\lambda - \psi_0) \right) \leq \left( \int dx_2 \cdots dx_N |\nabla (\psi_\lambda - \psi_0)|^2 \right)^{1/2}. \quad (52)$$

Finally, integrating,

$$\|\eta_\lambda\|_3 \leq c \int dx_1 \cdots dx_N |\nabla (\psi_\lambda - \psi_0)|^2 = c\|\psi_\lambda - \psi_0\|_{H^1}^2, \quad (53)$$

subscript $H^1$ indicating the Sobolev norm $\|f\|_{H^1}^2 = \|f\|_2^2 + \|\nabla f\|_2^2$. Now, $E_0(v_\lambda) \to E_0(v_0)$ and $\psi_\lambda \to \psi_0$, so

$$H_\lambda \psi_\lambda = E_0(v_\lambda) \psi_\lambda \to E_0(v_0) \psi_0 = H_0 \psi_0. \quad (54)$$

With potentials Kato-tiny relative to kinetic energy, this implies that $\psi_\lambda$ converges to $\psi_0$ in $H^2$ norm, a fortiori in $H^1$ norm.

### C. A justified feasible strategy?

Prop. 2 supports some members of the $\text{Str}_w^*$ family of strategies, for instance, $\text{Str}_{\text{min}}^*$: test $\Gamma(v^\circ, \rho_\lambda)$ for $\lambda = 1/2, 1/2^2, 1/2^3, \ldots$ until a result less than $\Gamma(v^\circ, \rho_0)$ is found, and take the corresponding $v_\lambda$ as the new input. Progress continues as long as isolated nondegenerate ground states are encountered. On the other hand, consider strategy $\text{Str}_{\text{rand}}^*$: select random direction $w = B'$ and minimize $\Gamma(v^\circ, \rho_\lambda)$ over $-1 \leq \lambda \leq 1$, where $(v + \lambda w, \rho_\lambda) \in \text{GP}_0$. Should not this, too, give progress, and if so, is Prop. 2 which does not prove that $\Delta v$ is a direction of particularly steep descent, really so impressive? On the surface, perhaps not, but it is reasonable to interpret Prop. 2 as saying that $\text{Str}_{\text{min}}^*$ “knows what it is doing”, and can therefore be expected to outperform $\text{Str}_{\text{rand}}^*$.

### 8. CONVERGENCE

Ideally a strategy would guarantee $\Gamma(v^\circ, \rho_\lambda) \to 0$. In light of the preceding, that is clearly a lot to ask, so we limit ourselves to a preliminary question. While $\Gamma(v^\circ, \rho_\lambda)$ does seem the best measure of closeness to a solution, it has the fatal flaw of not being evidently feasible. $\Delta v_\lambda$, on the other hand is feasible and measures how close $\psi_\lambda$ is to $v^\circ$. But, is it commensurate with $\Gamma(v^\circ, \rho_\lambda)$? With one new global regularity assumption, $(\text{Lip})$, we obtain an affirmative answer. Lieb’s $L^1 \cap L^3$ DFT theory has a Lipschitz continuous $E$, so the new assumption is certainly not overly strict.

**Proposition 3.** For a KS model obeying $(\text{Lip})$, so that $E$ has Lipschitz constant $C$,

$$\Gamma(v^\circ, \rho) - \Gamma(v, \rho) \leq (\|\rho\| + C)\|v - v^\circ\|.$$

In particular, if $(v, \rho) \in \text{GP}_0$, then

$$\Gamma(v^\circ, \rho) \leq (\|\rho\| + c)\|\Delta v\|.$$

**Proof.** By definition, $\Gamma(v^\circ, \rho) - \Gamma(v, \rho) = \langle v^\circ - v, \rho \rangle + E(v) - E(v^\circ)$. Since Lipschitz continuity of $E$ means that $|E(v) - E(v^\circ)| \leq C\|v - v^\circ\|$, the conclusion is immediate.

### 9. CONCLUSION

The bivariate perspective on Kohn-Sham iteration is more natural than the usual one which regards density as a variable but potential as a parameter. It naturally suggests new iterative strategies which are better justified at an abstract level, and shows the way to absolute measures of goodness-of-approximation.

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\[ \rho \sim \partial E_0(v) (= \rho) \]

GP

GP

\[ \rho^s \]

\[ [pE, \Pi](v) \]

\[ v, v+\Delta v, v, v^0 \]

\[ \Delta v \]