

# Lieb's most useful contribution to density functional theory?

Kieron Burke\*

Departments of Physics and Astronomy and of Chemistry,  
University of California, Irvine, CA 92697, USA

(Dated: February 14, 2022)

The importance of the Lieb-Simon proof of the relative exactness of Thomas-Fermi theory in the large- $Z$  limit to modern density functional theory (DFT) is explored. The principle, that there is a specific semiclassical limit in which functionals become local, implies that there exist well-defined leading functional corrections to local approximations that become relatively exact for the error in local approximations in this limit. It is argued that this principle might be used to greatly improve the accuracy of the thousand or so DFT calculations that are now published each week. A key question is how to find the leading corrections to any local density approximation as this limit is approached. These corrections have been explicitly derived in ridiculously simple model systems to ridiculously high order, yielding ridiculously accurate energies. Much analytic work is needed to use this principle to improve realistic calculations of molecules and solids.

*Submitted to book in honor of Elliott Lieb's 90th birthday, edited by Rupert L. Frank, Ari Laptev, Mathieu Lewin, & Robert Seiringer, published by EMS Press.*

**Lieb:** Elliott Lieb has made many seminal contributions to mathematical physics in general, and to density functional theory (DFT) in particular. Among the most famous are his establishment of the formal basis of DFT[1], the Levy-Lieb constrained search formulation[1, 2], and the Lieb-Oxford bound[3] and its extensions[4–6]. These and many others are celebrated in the current volume. But the main focus of this essay is an entirely different work, one that is much less well-known to modern practitioners of DFT.

**Lieb-Simon limit:** For many years, it was understood that the original DFT, that of Thomas and Fermi (TF)[7, 8], should become more accurate in a certain semiclassical limit. In this limit, both  $N$  and  $Z$  becomes large while their ratio remains fixed, with  $N$  being the number of electrons and  $Z$  being the total charge on the nuclei. The simplest case is the neutral atom,  $N = Z$ . For this problem, Lieb and Simon[9–11] proved that the relative error in the energy of a TF calculation vanishes in the limit. Moreover, the single-particle probability density  $n(\mathbf{r})$  approaches that of TF in a weak sense[11]. More generally, bond distances should be scaled at the same time (as  $Z^{1/3}$ ), to make this a non-trivial limit for all DFT calculations of atoms, molecules, and solids[12].

**Neutral atoms:** This Lieb-Simon (LS) limit has long been known in the physics community, and the expansion for neutral atoms has been performed to extract three terms:

$$E(Z) = -c_0 Z^{7/3} + \frac{1}{2} Z^2 - c_2 Z^{5/3} + \dots, \quad (1)$$

where  $c_0 \approx 0.768745$  and  $c_2 \approx 0.269900$  are fundamental constants that can be easily calculated to arbitrary accuracy [13–17]. TF theory produces exactly and only the first term, and the coefficient can be calculated to arbitrary accuracy by solving the TF equation[18], consistent with the LS proof. The second term is the Scott correction[19].

and can be deduced from the energy of an atom of non-interacting electrons, called a Bohr atom[20]. The last term combines two contributions, one from the local density approximation (LDA) exchange (2/11)[21, 22], and another from the gradient expansion of the non-interacting kinetic energy (9/11). The former coefficient was carefully studied by Schwinger[17], and a beautiful summary appears in Englert's book[13].

**Kohn-Sham DFT:** Modern DFT calculations use the Kohn-Sham scheme[23], in which only a small fraction of the total energy, called the exchange-correlation (XC) energy, needs to be approximated as a functional of the density. My group and collaborators have conjectured that the analogous statement for the XC energy is also true, namely that the local approximation for XC becomes relatively exact in this limit[24–26]. Many expectation values of quantum operators have useful local approximations in the density, such as the kinetic energy, but we reserve the term *the* local density approximation and acronym LDA for the XC energy. The claim is that the percentage error in LDA for XC vanishes as the LS limit is reached (not just the relative error in the total energy). In fact, this was 'proven' for exchange by Conlon in 1983[27], but the proof required a rounding of the Coulomb singularity. The Coulomb case was finally completed by Fefferman and Seco [28]. In fact, both X alone and C alone have this property. This is important because it has allowed study of the leading corrections to LDA, and comparisons made with modern generalized gradient approximations (GGAs). Insights derived from these studies have informed some of the most recent non-empirical functional approximations, such as PBEsol[29] and SCAN[30].

**Ionization potential:** The LS limit concerns total energies of systems, but interesting properties depend only on energy differences. A simple example of an energy difference is the ionization potential of an atom, being the difference in energy between the neutral atom and that with a single electron removed. This energy difference has the advantage that calculations need only be performed on spherical

\* kieron@uci.edu

potentials. We performed Hartree-Fock (HF) calculations for up to 3000 electrons, and compared with KS-DFT using LDA for  $X$  alone. We found that the dependence of the ionization potential across a row persisted even as  $Z \rightarrow \infty$ , but that nonetheless, within numerical accuracy, the LDA- $X$  calculations gave the exact result in the limit[31]. This is consistent with the proof of Solovej for Hartree-Fock (HF) theory that the ionization potential would remain finite in this limit[32]. At the exchange level, LDA and PBE[33] converge (within the limits of numerics) to the HF value (PBE is a particular popular GGA that reduces to LDA for a uniform gas). For XC, there is a small correction relative to HF, but PBE agrees with LDA, suggesting that even for the full Schrödinger equation, LDA is becoming relatively exact for the ionization potential in the LS limit. Moreover, a simple extended TF calculation from Englert's book[13], with a mild extension, appears to yield the correct limit of the ionization potential when averaged over rows of the periodic table.

**Leading corrections:** These are all numerical illustrations of conjectures. An obvious, vital question is: Can we derive these leading corrections analytically, even in such simple cases as spherical systems? For the present, the answer is no for XC. We have merely reversed-engineered some of their properties from simple atomic calculations[25, 34]. The next question then becomes: Can we derive the leading corrections under any conditions? The answer is yes, for the energy of non-interacting systems in one-dimension. By this, we mean making the equivalent of the TF approximation for the KS kinetic energy, and finding the leading corrections to this approximation in the LS limit. The answer also shows the underlying physics, explaining where and why these approximations become very accurate.

**Notation:** The rest of this article is devoted to 1D quantum systems with (mostly) smooth potentials, to which the LS limit also applies[35]. We show that, in such cases, we *can* derive the leading corrections to local density approximations. We use Hartree atomic units, with  $\hbar = m = 1$ , so that energies are in Hartree and distances in Bohr radii. Many more details and references to the original works can be found in a recent book chapter[36].

We denote the eigenvalues as  $\epsilon(j)$ , with  $j$  beginning at zero, and the sum of the first  $N$  eigenvalues as

$$E_N = \sum_{j=0}^{N-1} \epsilon(j). \quad (2)$$

Such a system can be thought of as 1D Kohn-Sham system where the potential would be the KS potential. The TF approximation is simply a local density approximation to the 1D kinetic energy of same spin electrons:

$$T^{\text{TF}}[n] = \frac{\pi^2}{6} \int dx n^3(x), \quad (3)$$

and the total energy must be minimized keeping the particle number  $N$  fixed.

**WKB approximation:** First we note that, in 1D, there exists the WKB approximation[37–39] which, in its simplest

form[40], states that

$$\int_{-\infty}^{\infty} dx p(\epsilon, x) = (j + \nu)\pi, \quad j = 0, 1, 2, \dots \quad (4)$$

where  $p(\epsilon, x) = \sqrt{2(\epsilon - v(x))}$  is the classical momentum with energy  $\epsilon$  at position  $x$ , taken to be zero if  $v(x) > \epsilon$ . Here  $\nu$  is the Maslov index[41], which is  $1/2$  for two turning points. We denote solutions as  $\epsilon^{(0)}(j)$ , the WKB eigenvalues. This formula yields the exact eigenvalues in the special cases of a particle in a box ( $\nu = 1$  due to two infinite barriers) and the harmonic oscillator ( $\nu = 1/2$ ).

**Simple example:** We use the Poschl-Teller (PT) well as a simple example,  $v(x) = -D/\cosh^2(x)$ , where  $D$  is the well-depth. The exact eigenvalues are

$$\epsilon(j) = -(\lambda - j)^2/2, \quad (5)$$

where  $\lambda = \sqrt{2D + 1/4} - 1/2$ , and  $j \leq \lambda$ . The WKB eigenvalues come out to be

$$\epsilon^{(0)}(j) = -(\lambda_0 - j)^2/2, \quad (6)$$

where  $\lambda_0 = \sqrt{2D} - 1/2$ . These are usually quite accurate, but not exact.

**Semiclassical limit:** Now we consider the semiclassical limit, which can be stated in several different related ways. The simplest way is to allow  $\hbar \rightarrow 0$ , but keep the chemical potential fixed. (For a spherical system, this produces  $Z \rightarrow \infty$ , keeping  $N/Z$  fixed. Neutrals are the special case of  $\mu = 0$ .) Thus the number of occupied levels grows in this limit. In terms of our parameters in 1D, this is equivalent to an expansion in  $1/\sqrt{D}$  keeping  $j/\lambda$  fixed, so that the WKB approximation becomes relatively exact for any individual eigenvalue. The WKB series can be calculated for a given potential. It is an expansion in even powers of  $\hbar$  and higher orders contain higher gradients of the potential. For the PT well, the leading correction to Eq. (6) is of order  $1/\sqrt{D}$ .

**Zero-order:** More importantly, for our purposes, is to consider the sum of the lowest  $N$  occupied levels. This is the total energy of  $N$  same-spin fermions sitting in this well. As  $\hbar \rightarrow 0$ , the spacing between levels becomes negligible, and this can be gotten by a simple integral over occupied WKB eigenvalues:

$$E_N^{(0)} = \int_0^{N-1} dj \epsilon^{(0)}(j) \quad (7)$$

Now, not only does this approximate answer become relatively exact in the semiclassical limit, but it is precisely the same as what the (1D non-interacting) TF approximation yields. This result was known at least as far back as 1956[42].

**Gradient expansion:** However, so far, all we have shown is consistency with the LS proof, in a far simpler case than the one of interest, i.e., we have shown that TF becomes relatively exact in this limit. Our goal is to find the leading correction to the approximation of Eq. (7), as this yields the leading corrections to TF, the local density approximation

to  $T$ , in this case. There is one case in which this can be (relatively) easily obtained, which is that of a slowly varying gas, as discussed by Hohenberg and Kohn[43] and others before them. In that case, an appropriate semiclassical expansion yields the correct answers. Samaj and Percus elegantly show[44] in 1D:

$$n(x) = \frac{p(x)}{\pi} \left[ 1 + \frac{v''(x)}{12p^4(x)} + \dots \right], \quad (8)$$

where  $p(x)$  is evaluated at  $\mu$ , the Fermi energy, determined by normalizing the density to  $N$  particles, and dashes denote spatial derivatives. Similarly, the kinetic energy density is

$$t(x) = \frac{p^3(x)}{2\pi} \left[ \frac{1}{3} + \frac{v''(x)}{4p^4(x)} + \dots \right]. \quad (9)$$

Inversion of Eq. (8) order-by-order in gradients of the potential and insertion in Eq. (9) yields the traditional gradient expansion

$$T[n] = T^{\text{TF}}[n] - \frac{1}{3}T^{\text{VW}}[n] + \dots, \quad (10)$$

where  $T^{\text{VW}}[n]$  is the von Weizsäcker kinetic energy[45]. This is for fully spin-polarized systems, but is trivially related to the unpolarized case via spin-scaling[46]. This is the 1D analog of the usual Kirzhnitz expansion[47] in 3D, the only difference being in the form of the TF term and the value (and sign) of the gradient correction.

*Next correction:* Returning now to finite systems, for any value of  $\hbar$ , one can solve self-consistently the Euler equation for the density of the system, and insert it into the total energy expression. Using the TF kinetic energy yields  $n^{\text{TF}}(x)$ , the TF approximation for the density. This yields

$$E^{\text{TF}} = T^{\text{TF}}[n^{\text{TF}}] + \int dx n^{\text{TF}}(x) v(x). \quad (11)$$

As the LS limit is approached,  $E^{\text{TF}}$  becomes identical to  $E_N^{(0)}$  of Eq. (7), exactly as required by the LS theorem.

But our interest is in the leading correction in that limit. A crucial point is that finite systems differ qualitatively from slowly varying gases, because they have classical turning points in 1D, i.e., places where the classical momentum appearing in Eq. (X) vanishes. They divide space into a region (or regions) where  $p > 0$ , called classically allowed, and the rest, which is classically forbidden (in quantum mechanics, the latter is called evanescent, and often involves exponentially decaying wavefunctions). In 3D, the separators is a surface, producing classically allowed regions around nuclei and forbidden regions outside. All molecules have forbidden regions, but slowly varying gases (and most real solids[48]) do not. This alters quantitatively the leading corrections to LDA in a way that no GGA can get right for both types of systems.

In our 1D examples, we see this explicitly in the presence of finite Maslov indices for one case, and zero indices for the other. Thus, the next term in the series for  $E_N$ , has two distinct contributions. The first is simply the correction due

to the next term in the WKB expansion for the eigenvalues, which depends on  $v''(x)$ , and gives

$$\Delta E_N^{(2a)} = \int_0^{N-1} dj \epsilon^{(2)}(j) \quad (12)$$

This is precisely the kind of term included in the gradient expansion. For a slowly varying gas, this will be the only contribution and the total energy will approach that of the gradient expansion as the variation in density is made slower. But for any system with turning points, there is a second contribution, due to the error in approximating the sum by an integral. This contribution is sensitive to the Maslov index, and can be found using the Euler-Maclaurin summation formula[49]. It has the well-known form

$$\Delta E_N^{(2b)} = \frac{1}{2} (\epsilon_{N-1}^{(0)} + \epsilon_0^{(0)}) \quad (13)$$

Such terms vanish in the slowly-varying gas, as the sum of Eq. (2) is in fact an integral in the thermodynamic limit. This contribution is precisely the difference between the standard, end-point, Riemann sum and the trapezoidal rule for integrals. The Riemann sum is first order accurate, but the trapezoidal rule is second order accurate. The higher-order corrections are discussed in Ref. [49].

Reference [50] was the first to isolate these two contributions, and calculate them for the Poschl-Teller well. Not only are the improvements very meager (and sometimes non-existent) if we only include the first term, but the improvements are spectacular once the right correction is included. Errors of the order of milliHartrees are obtained, and microHartrees if the next order is also included.

*Not Poschl-Teller:* Now this 1D case does indeed provide the answer we have sought. It is a recipe to extract the leading correction to the local approximation in the LS limit that can be applied to any (sufficiently smooth)  $v(x)$ , even if the dependence on  $v(x)$  has become quite implicit. In principle, we can convert functionals of the potential to those of the density[51, 52]. However, our use of the PT well is a little suspect, because in that case, the WKB series is absolutely convergent, whereas typically, we expect it to be only asymptotic. The next question becomes, will this work (and how well does it work) in a case where the series is asymptotic?

*Asymptotic analysis:* We answer this with asymptotic analysis, applied to another simple case, the linear well  $|x|$  in the half-space  $x > 0$ . Its eigenvalues are trivially related to zeroes of the Airy function. One can easily go through the same steps as performed above for the Poschl-Teller well, but it is obviously much more tricky to ascertain the best quality of results obtainable. In collaboration with Michael Berry, advanced asymptotic analysis was performed on the sum of eigenvalues [53]. Unlike the PT well, there are no explicit analytic formulas for the exact values. However, a comprehensive analysis of the asymptotic expansion to all orders takes the place of exact results. To understand the optimal performance achievable, given that the series are asymptotic, we calculated the sum of the first 10

energy levels, i.e.,  $E_{10}$ , as accurately as we could (using asymptotics, supersymptotics, and hypersymptotics), to find:

$$E_{10} \approx 81.513\,600\,174\,613\,249\,757\,575\,849\,944\,135\,041\,199 \quad (14)$$

to be contrasted with the exact value from Mathematica[53]

$$E_{10} = 81.513\,600\,174\,613\,249\,757\,575\,849\,944\,135\,032\,733 \quad (15)$$

This is some form of black magic. How can an approximation be right for 33 digits, and not be exact? We can even understand why we get 33 digits right! The optimal truncation order is typically  $\pi N$ , i.e., the order at which additions are least. Moreover, each order is smaller by a factor of  $1/N$ . Thus  $N = 10$ , and  $\pi N = 31$ . Finally, hypersymptotics reduced our errors by two more orders of magnitude.

Of course, this tour-de-force is not designed to yield practical approximations. No practical DFT electronic structure calculation can match this accuracy. It is purely designed to show that we understand the basic principles, and just how powerful the correct asymptotic expansion can be when fully understood.

*Subdominant terms:* A further difficulty can occur when there are complex turning points for the potential. These generate subdominant terms (the beginning of a trans-series) that are missed by the standard WKB series. The simplest such example is the quartic oscillator,  $x^4$ . We recently published many benchmark numbers for this potential (generalized to include a quadratic term)[54]. We have also completed the asymptotic sum analysis of the WKB series plus the leading sub-dominant corrections[55]. While more complicated, it is relatively straightforward to find the sub-dominant corrections to the asymptotic sums, with similarly spectacular results (although not quite as spectacular, with errors as large as  $10^{-21}$  for the sum of 10 levels).

*The road ahead:* So, where does this all leave us, and what is the path forward? The crucial point is that it *is* possible to derive the leading corrections to the LS limit in these simple cases. To generalize these results to a point where they can be practically useful, we must (a) go from one to three dimensions (b) go from the kinetic energy to the exchange and exchange-correlation energies (c) include Coulomb attractions to nuclei as well as Coulomb repulsion between electrons, and (d) be able to handle multi-centered problems, not just spherical systems. We are currently pursuing multiple avenues that take steps in

these directions. Each has its own mathematical challenges, where help would be much appreciated.

*Hard math:* Perhaps the most difficult problem is performing sums over more than a single index. This was looked at briefly in a very simple case in Ref. [53]. In that case, the number staircase for particles that are free in two-dimensions was considered, with periodic boundary conditions (i.e., particles on a torus). Moreover, the relative periods in the two directions was chosen as  $\sqrt{2}$ , making them incommensurate, and the appearance of new levels pseudorandom. The results found could be interpreted in two different ways. The asymptotic sums were found to yield results as good as (and almost indistinguishable from) those of the individual levels. Given the difficulty of such problems, this could be regarded as a very promising sign. On the other hand, the results were no better than the results for individual eigenvalues, so more study needs to be done to see if better results can be achieved.

A review of asymptotic series that appeals to physical scientists is that of Boyd[56]. A rigorous review for mathematicians is the book of Costin[57]. There has been recent interest in this area from the perspective of particle physics, in the language of solitons, resurgence, and trans-series[58–60].

*Conclusions:* In conclusion, it has been established that, in very simple cases, it *is* possible to derive general formulas for the leading corrections to local density approximations, and that these corrections can often be extremely accurate. It is conjectured that if these corrections could be found for the exchange-correlation energy of Kohn-Sham DFT, they would yield approximate functionals of far higher accuracy than those in current use. However, there are many challenges in generalizing these results, chief among them being the ability to sum over more than one index and to handle degeneracies. On the more traditional end, a rigorous proof that XC becomes relatively exact in the LS limit would be most welcome. Any results in this and related areas from Elliott or his many friends, preferably before his hundredth birthday, would be most appreciated.

*Acknowledgements:* This essay is dedicated to Elliott Lieb on the occasion of his 90th birthday. He is that rarest of mathematical physicists, namely one whose results are quite often directly and immediately useful to practitioners. I thank the NSF for grant CHE-1856165 for support, and Mathieu Lewin, John Perdew, and especially Carlos Garcia-Cerveza, for helpful comments.

This essay is a description of physics. Any resemblance to mathematical rigor, real or assumed, is entirely coincidental. No theorems were violated in the writing of this manuscript (I hope).

---

- [1] E. H. Lieb, "Density functionals for coulomb systems," *Int. J. Quantum Chem.*, **24**, 243 (1983).
- [2] M. Levy, "Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the  $v$ -representability problem,"

- Proceedings of the National Academy of Sciences of the United States of America, **76**, 6062 (1979).
- [3] E. H. Lieb and S. Oxford, "Improved lower bound on the indirect Coulomb energy," *International Journal of Quantum Chemistry*, **19**, 427 (1981).

[4] M. Lewin and E. H. Lieb, "Improved Lieb-Oxford exchange-correlation inequality with a gradient correction," *Phys. Rev. A*, **91**, 022507 (2015).

[5] D. V. Feinblum, J. Kenison, and K. Burke, "Communication: Testing and using the Lewin-Lieb bounds in density functional theory," *The Journal of Chemical Physics*, **141**, 241105 (2014).

[6] L. A. Constantin, A. Terentjevs, F. Della Sala, and E. Fabiano, "Gradient-dependent upper bound for the exchange-correlation energy and application to density functional theory," *Phys. Rev. B*, **91**, 041120 (2015).

[7] L. H. Thomas, "The calculation of atomic fields," *Math. Proc. Camb. Phil. Soc.*, **23**, 542 (1927).

[8] E. Fermi, "Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente (A statistical method for the determination of some atomic properties and the application of this method to the theory of the periodic system of elements)," *Zeitschrift für Physik A Hadrons and Nuclei*, **48**, 73 (1928).

[9] E. Lieb and B. Simon, "Thomas-Fermi Theory Revisited," *Phys. Rev. Lett.*, **31**, 681 (1973).

[10] E. H. Lieb, "The stability of matter," *Rev. Mod. Phys.*, **48**, 553 (1976).

[11] E. H. Lieb, "Thomas-Fermi and related theories of atoms and molecules," *Rev. Mod. Phys.*, **53**, 603 (1981).

[12] E. H. Lieb and B. Simon, "The Thomas-Fermi theory of atoms, molecules and solids," *Advances in Mathematics*, **23**, 22 (1977).

[13] B.-G. Englert, "Semiclassical theory of atoms," *Lec. Notes Phys.*, **300** (1988).

[14] B.-G. Englert and J. Schwinger, "Semiclassical atom," *Phys. Rev. A*, **32**, 26 (1985).

[15] P. Elliott, D. Lee, A. Cangi, and K. Burke, "Semiclassical Origins of Density Functionals," *Phys. Rev. Lett.*, **100**, 256406 (2008).

[16] J. Schwinger, "Thomas-Fermi model: The leading correction," *Phys. Rev. A*, **22**, 1827 (1980).

[17] J. Schwinger, "Thomas-Fermi model: The second correction," *Phys. Rev. A*, **24**, 2353 (1981).

[18] D. Lee, L. A. Constantin, J. P. Perdew, and K. Burke, "Condition on the Kohn-Sham kinetic energy and modern parametrization of the Thomas-Fermi density," *J. Chem. Phys.*, **130**, 034107 (2009).

[19] J. Scott, "The binding energy of the Thomas-Fermi atom," *Philos. Mag.*, **43**, 859 (1952).

[20] O. J. Heilmann and E. H. Lieb, "Electron density near the nucleus of a large atom," *Phys. Rev. A*, **52**, 3628 (1995).

[21] F. Bloch, "Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfähigkeit," *Zeitschrift für Physik*, **57**, 545 (1929).

[22] P. A. M. Dirac, "Note on Exchange Phenomena in the Thomas Atom," *Mathematical Proceedings of the Cambridge Philosophical Society*, **26**, 376 (1930).

[23] W. Kohn and L. J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects," *Phys. Rev.*, **140**, A1133 (1965).

[24] E. S. J. P. Perdew, L. A. Constantin and K. Burke, "Relevance of the slowly-varying electron gas to atoms, molecules, and solids," *Phys. Rev. Lett.*, **97**, 223002 (2006).

[25] P. Elliott and K. Burke, "Non-empirical derivation of the parameter in the B88 exchange functional," *Canadian Journal of Chemistry*, **87**, 1485 (2009).

[26] K. Burke, A. Cancio, T. Gould, and S. Pittalis, "Locality of correlation in density functional theory," *The Journal of Chemical Physics*, **145**, 054112 (2016).

[27] J. G. Conlon, "Semi-classical limit theorems for Hartree-Fock theory," *Communications in Mathematical Physics*, **88**, 133 (1983).

[28] L. A. Fefferman, Charles L. Seco, *Bull. Amer. Math. Soc. (N.S.)*, **23**, 525 (1990).

[29] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, "Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces," *Phys. Rev. Lett.*, **100**, 136406 (2008).

[30] J. Sun, A. Ruzsinszky, and J. P. Perdew, "Strongly Constrained and Appropriately Normed Semilocal Density Functional," *Phys. Rev. Lett.*, **115**, 036402 (2015).

[31] L. A. Constantin, J. Snyder, J. P. Perdew, and K. Burke, "Ionization potential in the limit of large atomic number," *J. Chem. Phys.*, **133**, 241103 (2011).

[32] J. Solovej, "The ionization conjecture in Hartree-Fock theory," *Ann. Math.*, **158**, 509 (2003).

[33] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Phys. Rev. Lett.*, **77**, 3865 (1996), *ibid.* **78**, 1396(E) (1997).

[34] A. Cancio, G. P. Chen, B. T. Krull, and K. Burke, "Fitting a round peg into a round hole: asymptotically correcting the generalized gradient approximation for correlation," *The Journal of Chemical Physics*, **149**, 084116 (2018).

[35] S. Fournais, M. Lewin, and J. P. Solovej, "The semi-classical limit of large fermionic systems," *Calculus of Variations and Partial Differential Equations*, **57**, 105 (2018).

[36] P. Okun and K. Burke, "Semiclassics: The hidden theory behind the success of DFT," *arXiv:2105.04384* (2022).

[37] G. Wentzel, "Eine Verallgemeinerung der Quantenbedingungen für die Zwecke der Wellenmechanik," *Z. Phys.*, **38**, 518 (1926).

[38] H. Kramers, "Wellenmechanik und halbzählig Quantisierung," *Z. Phys.*, **39**, 828 (1926).

[39] L. Brillouin, "La mecanique ondulatoire de Schrödinger: une methode generale de resolution par approximations successives," *Compt. Rend.*, **183**, 24 (1926).

[40] D. J. Griffiths, *Introduction to Quantum Mechanics* (Pearson Prentice Hall, Upper Saddle River, 2005).

[41] V. Maslov and V. Fedoriuk, *Semi-Classical Approximation in Quantum Mechanics*, Mathematical Physics and Applied Mathematics (Springer Netherlands, 2001).

[42] N. H. March and J. S. Plaskett, "The Relation between the Wentzel-Kramers-Brillouin and the Thomas-Fermi Approximations," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, **235**, 419 (1956).

[43] P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas," *Phys. Rev.*, **136**, B864 (1964).

[44] L. Samaj and J. K. Percus, "Recursion representation of gradient expansion for free fermion ground state in one dimension," *The Journal of Chemical Physics*, **111**, 1809 (1999).

[45] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990).

[46] G. Oliver and J. Perdew, "Spin-density gradient expansion for the kinetic energy," *Phys. Rev. A*, **20**, 397 (1979).

[47] D. Kirzhnits, "Quantum corrections to the Thomas-Fermi equation," *Sov. Phys. JETP*, **5**, 64 (1957).

[48] A. D. Kaplan, S. J. Clark, K. Burke, and J. P. Perdew, "Calculation and interpretation of classical turning surfaces

in solids," *npj Computational Materials*, **7**, 25 (2021).

[49] K. Burke, "Deriving approximate functionals with asymptotics," *Faraday Discuss.*, **224**, 98 (2020).

[50] K. Burke, "Leading correction to the local density approximation of the kinetic energy in one dimension," *The Journal of Chemical Physics*, **152**, 081102 (2020).

[51] A. Cangi, D. Lee, P. Elliott, K. Burke, and E. K. U. Gross, "Electronic Structure via Potential Functional Approximations," *Phys. Rev. Lett.*, **106**, 236404 (2011).

[52] A. Cangi, E. K. U. Gross, and K. Burke, "Potential functionals versus density functionals," *Phys. Rev. A*, **88** (2013).

[53] M. V. Berry and K. Burke, "Exact and approximate energy sums in potential wells," *Journal of Physics A: Mathematical and Theoretical*, **53**, 095203 (2020).

[54] P. Okun and K. Burke, "Uncommonly accurate energies for the general quartic oscillator," *International Journal of Quantum Chemistry*, **121**, e26554 (2021).

[55] P. Okun and K. Burke, "Asymptotics of eigenvalue sums when some turning points are complex," in preparation (2022).

[56] J. P. Boyd, "The Devil's Invention: Asymptotic, Superasymptotic and Hyperasymptotic Series," *Acta Applicandae Mathematica*, **56**, 1 (1999).

[57] O. Costin, *Asymptotics and Borel Summability (1st ed)* (Chapman and Hall/CRC., 2008).

[58] G. V. Dunne and M. Ünsal, "Uniform WKB, multi-instantons, and resurgent trans-series," *Phys. Rev. D*, **89**, 105009 (2014).

[59] G. V. Dunne and M. Ünsal, in *Resurgence, Physics and Numbers*, edited by F. Fauvet, D. Manchon, S. Marmi, and D. Sauzin (Scuola Normale Superiore, Pisa, 2017) pp. 249–298, ISBN 978-88-7642-613-1.

[60] O. Costin and G. V. Dunne, "Convergence from divergence," *Journal of Physics A: Mathematical and Theoretical*, **51**, 04LT01 (2017).