Electronic structure from conditional probabilities

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(Dated: Monday 13th July, 2020)

Accurate ground-state energies are the focus of most electronic structure calculations. Such energies can, in principle, be extracted from a sequence of density functional calculations of conditional probabilities (CP-DFT), without approximating the energy directly. Simple CP approximations yield useful and accurate results for a broad range of systems: two-electron ions, the hydrogen dimer, and the uniform gas at all temperatures. CP-DFT has no self-interaction error for one electron, and correctly dissociates H2, both major challenges in standard density functional theory. Orbital free CP-DFT may be ideal for warm dense matter simulations.

Modern electronic structure calculations usually focus on finding accurate ground-state energies, as so many properties of a molecule or a material depend on this ability [1]. Wavefunction-based methods, such as coupled-cluster theory [2,3] or quantum Monte Carlo (QMC) [4,5], directly yield energies. Kohn-Sham (KS) density functional theory (DFT) [6] incorporates the many-electron problem into the exchange-correlation (XC) energy, which must be approximated as a functional of spin densities. Hundreds of distinct XC approximations are available in standard codes [7], reflecting the tremendous difficulty in finding general, accurate approximations. Recently, KS-DFT at finite temperatures, based on the Mermin theorem [8], has been tremendously successful in simulations of warm dense matter [9,10].

But XC energies are determined by the joint probability density for finding electrons at two points. This pair density can always be written as

\[ P(r, r') = n(r) \tilde{n}_r(r'), \]

where \( n(r) \) is the single particle density, and \( \tilde{n}_r(r') \) is the conditional probability (CP) density of finding an electron at \( r' \), given an electron at \( r \). The standard exact KS potential of DFT, \( v_s[n](r) \), is defined to yield \( n(r) \) in an effective fermionic non-interacting problem [11]. Likewise, a conditional probability KS potential (CPKS), \( v_s[\tilde{n}_r](r') \), yields \( \tilde{n}_r(r') \) from such a KS calculation with \( N-1 \) electrons. Because standard KS-DFT calculations usually yield highly accurate densities [12], an accurate CPKS potential should yield highly accurate XC energies.

Under many circumstances (such as well-separated points or higher temperatures), the CP potential is simply approximated by adding 1/|r − r'| to the external potential, the repulsion due to the missing electron as if it were a classical point particle. We call this a blue electron (i.e. distinguishable from all others), recalling the Percus test particle of classical statistical mechanics [13]. However, at small separations, the electron-electron cusp condition [14], implies adding only 1/2 this potential (the 2 is due to the reduced mass). We interpolate between these limits in our calculations.

![FIG. 1. CP (blue) and exact (black) energies: (a) XC energy per particle in uniform gas at increasing Wigner-Seitz radii (rs) and T = 0, (b) binding energy curve for H2, and (c) XC free energy per particle at rs = 1 as a function of reduced temperature (T_F is the Fermi temperature) for three different approximations: KS (Kohn-Sham), TF (Thomas-Fermi), and CL (classical). Exact from Ref. [15] in (a), Ref. [16] in (b), and Ref. [17] in (c).]  

Hartree atomic units used throughout.

Representative results are shown in Fig. 1. For the uniform electron gas at zero temperature, our CP potential interpolation is extremely accurate. We added a strong repulsion for \( rs < 1 \), to recover the exchange limit. The middle panel shows the H2 binding curve, where the inclusion of the electron-electron cusp is vital. Unlike
semi-local DFT, CP-DFT dissociates the molecule correctly, remaining spin-unpolarized throughout. The bottom panel (c) shows that CP can be used at all temperatures $T$. As $T$ is raised from very low to very high, the CP-DFT error never exceeds 20% and vanishes in the high temperature limit. Moreover, results of orbital-free Thomas-Fermi, and even classical, CP calculations agree reasonably with both KS-CP and the accurate results for all $T > T_F$.


to keep the ground-state density $n(r)$ fixed [17]. The XC energy is:

$$E_{XC} = \frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{\hat{v}_\lambda^r(r') - n(r)}{|r - r'|}, \quad (3)$$

with $\hat{v}_\lambda^r(r') - n(r)$ being the $\lambda$-dependent XC hole, defined via the $\lambda$-dependent generalization of Eq. [1]. Setting $\lambda = 1$ in Eq. [3] yields $U_{XC}$, the potential contribution to XC. The integral over $\lambda$ is called the adiabatic connection.

Denote $\hat{v}_\lambda[n](r)$ as the unique one-body ground-state density for electron repulsion $\lambda/|r - r'|$. The conditional probability potential is

$$\hat{v}_\lambda(r'|r) = v[n](r') + \Delta\hat{v}_\lambda^r[n](r'), \quad (4)$$

being the unique potential whose ground-state density for Coulomb interacting electrons yields the exact $\lambda$-dependent CP density. The CP-KS potential is found self-consistently:

$$\hat{v}_\lambda^r(r'|r) = v_\lambda[n](r') = v[n](r') + \hat{v}_\lambda^r[n](r'), \quad (5)$$

where $v_{\text{HXC}}$ is the Hartree-XC potential [11]. Thus knowledge of the CP correction potential, $\Delta\hat{v}_\lambda^r[n](r')$ in Eq. [4] allows a self-consistent KS calculation for the exact CP density. Uniqueness of the CP potential is guaranteed by the HK theorem. As $\hat{n}_\lambda^r(r')$ is non-negative, normalized to $N - 1$, and found from a wavefunction, it is in the standard space of densities, for which we routinely assume KS potentials exist [18, 19].

The above equations are for pure density functionals, and their analogs for spin-density functionals are straightforward (but cumbersome). Decades of research in DFT can be applied to the study of CP densities and potentials, yielding many exact conditions. For example, at $\lambda = 0$ where the exchange hole is never positive,

$$\hat{n}_\lambda^r(r') \leq n(r'). \quad (6)$$

The CP densities satisfy a complementarity principle:

$$\hat{n}_\lambda^r(r') = \frac{n(r)}{n(r')^\lambda} \hat{n}_\lambda^r(r), \quad (7)$$

which is Bayesian, and may be amenable to modern machine-learning methods. The electron coalescence cusp condition requires

$$\left. \frac{\partial \hat{n}_\lambda^r(r, u)}{\partial u} \right|_{u=0} = \lambda \hat{n}_\lambda^r(r), \quad (8)$$

where $u = r' - r$ and the left-hand side has been spherically averaged over $r + u$ [20]. For $N = 1$, $\hat{n}_\lambda^r(r') = 0$, there is no self-interaction error [21]. If $N = 2$, the CP density has just one electron:

$$\hat{\phi}_\lambda^r(r') = \sqrt{\hat{n}_\lambda^r(r')} = \sqrt{\frac{2}{n(r)}} \Psi^\lambda r, r', \quad (9)$$

yielding

$$\hat{v}_\lambda^r(r'|r) - c_\lambda^r = \frac{1}{2} \nabla^2 \Psi^\lambda(r, r'), \quad (10)$$

where $c_\lambda^r$ is the eigenvalue of the CPKS potential. Because the wavefunction satisfies the Schrödinger equation, we find

$$\Delta \hat{v}_\lambda^r(r'|r) + \hat{v}_\lambda^r(r|r') = \lambda \frac{1}{|r - r'|} - E^\lambda, \quad (11)$$

where $\Delta \hat{v}_\lambda^r(r'|r) = \hat{v}_\lambda^r(r'|r) - v^\lambda[n](r') - c_\lambda^r$.

Approximations: To perform a CP-DFT calculation, we need a general-purpose approximation to the CP potential, $\Delta\hat{v}_\lambda^r(r')$. We generalize Ref. [22], to arbitrary $\lambda$. The starting point is

$$\Psi^\lambda(1 \ldots N) = \sqrt{\frac{n(r_1)}{N}} \hat{\Psi}^\lambda(2 \ldots N). \quad (12)$$

$\hat{\Psi}^\lambda$ is not antisymmetric under interchange of the electrons, but is uniquely defined by Eq. [12] and $n_\lambda^r$ is its density. Ref. [22] finds an effective equation for $n(r)$, but also yields an apparent Schrödinger equation for $\Psi^\lambda$ with Hamiltonian:

$$\hat{H}^\lambda = H^\lambda(2 \ldots N) + \sum_{j=2}^N \frac{\lambda}{|r - r_j|} + v_{\text{nuc}}^{\lambda}(2 \ldots N|r) \quad (13)$$

where $H^\lambda(2 \ldots N) \ldots$ is the sum of the kinetic and one-body potential energies of these electrons in potential $v(r_j)$, and $v_{\text{nuc}}^{\lambda}$ includes gradients of $\hat{\Psi}^\lambda$ with respect to $r$. This is not an eigenvalue equation that you solve with given boundary conditions. It is a differential equation satisfied by $\Psi^\lambda$, defined by Eq. [12] This is an example of the exact factorization technique for studying nuclear dynamics, but can also be applied to the pure electronic problem [23]. Conditional wavefunctions are not always the lowest eigenstate if one treats this as an eigenvalue
problem [24]. Worse, \( v_{\text{nuc}}^\lambda \) depends on \( N - 1 \) coordinates simultaneously, so the usual theorems of DFT cannot be applied.

But, we can use this analysis to make a good approximation. Drop \( v_{\text{nuc}}^\lambda \) and the corresponding differential equation now matches a standard \( N - 1 \)-electron problem, with

\[
\Delta \tilde{v}_{\mathbf{r}}^\lambda[n](\mathbf{r}') \approx \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|}. \tag{14}
\]

We call this a blue electron approximation, as it treats one electron as distinguishable from all others (painted blue), and so adds a Coulomb repulsion to the one-body potential. This becomes exact for large \( r \), as Ref. [22] shows \( \tilde{\Psi}_\mathbf{r} \) collapses to the \( (N - 1) \)-electron ground state. It is also exact in the high temperature, classical, and some strongly correlated limits. But a pure blue approximation must fail at small separations, as it yields a cusp that is too large by a factor of 2. Instead, we interpolate with a local density approximation

\[
\Delta \tilde{v}_{\mathbf{r}}^\lambda[n](\mathbf{r}') \approx \frac{\lambda}{2|\mathbf{r} - \mathbf{r}'|} \left( 1 + \text{Erf} \left( \frac{|\mathbf{r} - \mathbf{r}'|}{r_s(n(\mathbf{r}))} \right) \right), \tag{15}
\]

where \( r_s = (3/(4\pi n))^{1/3} \) is the Wigner-Seitz radius at the reference point. Fig. 1(a) and (b) use Eq. 15 combined with standard DFT approximations for \( v_{\text{XC}} \), Fig. 1(c) uses Eq. 14.

**Uniform electron gas:** The \( N \)-electron density is trivially a constant, and the one-body potential vanishes. The CP calculation is for \( N - 1 \) electrons in a KS potential:

\[
v_s(r) = \Delta \tilde{v}(r) + \int d^3r' \frac{n(r') - n_0}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{LDA}}^{\text{XC}}[n](\mathbf{r}), \tag{16}
\]

where \( n_0 = N/V \) and

\[
\Delta \tilde{v}(r) = \Delta \tilde{v}_0^{(\lambda=1)}(n_0, r) + A(r_s)e^{-r^2/2\sigma(r_s)^2}. \tag{17}
\]

The second term is added to recover the correct high-density limit, i.e., the simple \( n^{4/3} \) exchange energy. If we run for many \( r_s \) values, we can perform the adiabatic connection integral by integrating over \( r_s \), so we need only \( \lambda = 1 \). The XC potential is from [25]. The strength and range parameters of the added Gaussian potential are fitted to [25] for \( r_s = 0.02 \), where exchange dominates. The density is found self-consistently in a sphere using Fermi-surface smearing \((T = 0.05T_F)\). Imposing zero density flux through the surface of the sphere minimizes boundary effects. We find \( N = 512 \) is sufficient for convergence. Further details will appear in a forthcoming paper.

Fig. 2 shows the hole density compared to that given by the parameterization of the uniform gas XC hole [26]. The agreement is very good, with the lowest accuracy from the on-top region, which has very little weight in the XC energy.

**Atoms and molecules:** We applied Eq. 15 to highly accurate calculations of 2-electron systems. These calculations were done using a new type of basis function called gausslets [27, 28] which are tailored for density matrix renormalization group calculations [29] and based on wavelets. Gausslets resemble a variable-spaced real-space grid. The two-electron Hamiltonian terms have only two indices, \( V_{ij} \), unlike the four indices needed in a standard basis. The grid-like structure make CP calculations easy to implement. A blue electron sitting at a point in space sits on a gausslet, \( i \), located at its reference, \( r_i \). The repulsive one-electron potential of Eq. 14 at \( i \) is simply row \( i \) of \( V_{ij} \). Integration likewise becomes point-wise sums. Recent innovations add a Gaussian basis to better describe atomic core behavior, further described in a forthcoming work. We used no more than 2000 gausslets with errors in total energies for \( Z = 1 \) and \( Z = 2 \) below 0.1 mH. To find the conditional probability using Eq. 15 we find the ground state of an \( N \times N \) matrix with the Lanczos algorithm [30] and repeat \( N \) times. Gausslets make an excellent basis for CP calculations, but in any basis, CP calculations are receptive to parallel computing, as each value of \( r \) and \( \lambda \) can be computed independently.

We present results for 2-electron ions in Table [1]. We have performed the double integral over \( r \) and \( r' \) to find the potential contribution to correlation, \( U_C \). The virial theorem for atoms (relating the total energy to total kinetic energy, \( E = -T \)) allows us to deduce \( E_C \), without needing to perform the adiabatic connection. For \( \text{He} \), the \( E_C \) error is just 8 mH, and is only 20% for both \( U_C \) and \( E_C \). As \( Z \to \infty \), the CP calculation correctly yields a finite value.

The virial trick only works for Coulomb-interacting atoms and molecules at equilibrium. Otherwise, we need to perform the adiabatic connection integral. For \( N = 2 \), we know the exact result as \( \lambda \to 0 \) (exchange limit), where \( \tilde{\Psi}_\mathbf{r}^{\lambda=0}(\mathbf{r}') = n(\mathbf{r}')/2 \). By definition, for 2-electrons we have

\[
\tilde{\Psi}_s^\lambda(\mathbf{r}'|\mathbf{r}) = v_s[n](\mathbf{r'}) - \lambda v_{\text{hh}}[n](\mathbf{r'}) - v_C^\lambda[n](\mathbf{r'}) + \Delta \tilde{v}_s^\lambda(\mathbf{r}'|\mathbf{r}). \tag{18}
\]

In practice, obtaining \( v_C^\lambda[n](\mathbf{r'}) \) is difficult, and we
TABLE I. Results for 2-electron Helium-like ions, where the virial $E_{C}^{\text{Virial}}$ is derived from the virial theorem for atoms using exact $T_{s}$ from Ref. 31.

| $Z$ | $E_{X}$ | $V_{s}^{\text{CP}}$ | $U_{C}^{\text{CP}}$ | $U_{C}^{\text{Exact}}$ | virial $E_{C}^{\text{CP}}$ | $E_{C}^{\text{Exact}}$ |
|-----|---------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 1.0 | -0.3810 | 0.2828              | -0.0982             | -0.6098             | -0.0562             | -0.0420             |
| 2.0 | -1.0245 | 0.9294              | -0.0951             | -0.7868             | -0.0503             | -0.0421             |
| 3.0 | -1.6510 | 1.5518              | -0.0992             | -0.8322             | -0.0515             | -0.0435             |
| 4.0 | -2.2766 | 2.1748              | -0.1017             | -0.8857             | -0.0523             | -0.0443             |
| 6.0 | -3.5270 | 3.4225              | -0.1045             | -0.8881             | -0.0534             | -0.0452             |

The approximate function

$$\tilde{v}_{\lambda}^{A}(r'|r) = \begin{cases} v_{\lambda}[n](r') & , \lambda = 0 \\ v(n)[r'] + (1 - \lambda)v_{\infty}[n](r') + \Delta v_{\lambda}^{A}(r'|r) & \end{cases}$$

(19)

to recover the exchange limit exactly. In the following calculation for $H_{2}$, we utilize the interpolated blue approximation, Eq. 15 for $\Delta \tilde{v}_{\lambda}^{A}(r'|r)$ and the exact density $n(r')$ throughout. We run for $\lambda \in \{0, 0.1, 0.3, 0.5, 0.7, 1.0\}$, and fit to a first-order Padé approximant, which is integrated analytically.

| $R$ | $E_{X}$ | $V_{s}^{\text{Blue}}$ | $U_{C}^{\text{Blue}}$ | $U_{C}^{\text{Exact}}$ | $E_{C}^{\text{Blue}}$ | $E_{C}^{\text{Exact}}$ |
|-----|---------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 1.0 | -0.7472 | 0.6688              | -0.0785             | -0.0732             | -0.0433             | -0.0400             |
| 2.0 | -0.5698 | 0.4720              | -0.0978             | -0.0835             | -0.0587             | -0.0478             |
| 4.0 | -0.4323 | 0.2576              | -0.1747             | -0.1692             | -0.1359             | -0.1318             |
| 8.0 | -0.3749 | 0.1241              | -0.2497             | -0.2499             | -0.2445             | -0.2477             |

TABLE II. $H_{2}$ energies versus $R$, where $E_{C}^{\text{Blue}}$ is computed from Eq. 19 with the exact density.

FIG. 3. $U_{c}(R)$ from $H_{2}$. The pure blue electron approximation, Eq. 14 (purple), half that potential (orange), our interpolation, Eq. 15 using exact $n(r)$ (blue), and exact (black). The interpolation error never exceeds 20%.

The binding curve for $H_{2}$ as a function of bond length is shown in Fig 1(b), with components given in Table II. Fig. 3 shows $U_{c}(R)$ for 3 distinct choices of CP potential. As $R \to \infty$, any version of the blue electron approximation becomes accurate. Consider what happens as the bond is stretched. The exact wavefunction has Heitler-London form:

$$\Psi^{\lambda}(r_{1}, r_{2}) = \frac{1}{\sqrt{2}} (\phi_{A}(r_{1}) \phi_{B}(r_{2}) + \phi_{B}(r_{1}) \phi_{A}(r_{2}))$$

(20)

where $\phi_{A}$ and $\phi_{B}$ are atomic orbitals localized on each of the two protons. This yields a conditional density:

$$n_{\lambda}^{A}(r') = n_{B}(r'), \quad r \text{ near } A$$

(21)

and vice versa, for all $\lambda \neq 0$. Thus the Coulomb energy of the pair density vanishes due to the lack of overlap, and each atomic region correctly yields a one-electron energy of a separate hydrogen atom. CP-DFT is an exact theory for bond dissociation, unlike the on-top hole theory of Ref. 33.

Hooke’s atom consists of two Coulomb repelling electrons in a harmonic potential of force constant $k$ [34]. At $k = 1/4$, the density is known analytically, and at $r = 0$, the exact $\tilde{v}_{\lambda}^{A}(r'|r)$ is radial. In Fig. 4 we compare the approximations in Eqs. 14 and 15 with the exact CP potential and the resulting densities $n_{\lambda}^{A}(r')$. Note the accuracy of the blue approximation for large $r'$, and the cusps as $r' \to r$ in the exact and approximate CP densities.

Finite temperatures: Possibly, the most important application of CP DFT is for thermal equilibrium in warm dense matter [12]. While thermal KS-DFT calculations have been very successful, finding consistent temperature-dependent approximations is more difficult than at zero temperature [35]. Moreover, calculations using KS solvers eventually fail at extremely high temperatures, due to convergence difficulties with orbital sums.

For finite temperatures, Eq 3 translates to $F_{X C}$, the XC contribution to the Helmholtz free energy, which folds in entropic contributions [8, 36]. To find accurate CP densities, we solve the KS equations with finite temperature...
occupations. (Thermal corrections to \(\epsilon_{xc}\) have been argued to have little effect on the orbitals [37].) In Fig. 1 (c), we showed results for the potential XC free energy at \(r_s = 1.0\) for a wide range of temperatures. The solid line displays the analytical parameterization (Ref. [16]). The KS CP approximation mildly overestimates \(f_{xc}\) for \(t = T/T_F\) between about 0.2 and 9, beyond which it fails to converge.

For higher temperatures, we performed a much simpler CP calculation using the Thomas-Fermi (TF) approximation [38]–[39], often employed in warm dense matter [40]–[41], and implementing the simple blue approximation, Eq. [14]. We first solved the TF equation at \(T = 0\). This was used to initiate iterations for a full numerical solution. We make a simple interpolation of Perrot’s [42] accurate parameterization of the Helmholtz free energy density \(f_0(n)\) of the uniform non-interacting electron gas constructed to yield the correct \(T = 0\) and (classical) \(T \to \infty\) limits:

\[
f_0(n) = k_B T n \left( \ln(y) - c + a y^{\frac{3}{2}} \right), \tag{22}
\]

where \(y = \pi^2 n / \sqrt{2 \left( k_B T \right)^{3/2}}, c = 1 - \ln(2 / \sqrt{\pi}),\) and \(a = 9(2/3)^{1/3}/10\). The Fermi temperature is given by \(k_B T_F = (3\pi^2 n)^{2/3} / 2\). As \(T \to 0\), \(f_0(n) = 3n k_B T_F / 5\) as required. TF theory corresponds to minimizing the Mermin [8] grand potential functional ignoring XC and making the local density approximation \(F[n] = \int d^3 r f_0(n(r))\) for the non-interacting Helmholtz free energy.

**Classical connection:** In the classical limit TF theory reduces to the Poisson-Boltzmann (PB) theory used to treat electrical double layers and many other properties of electrolyte solutions and ionic liquids [43]. In the high temperature limit we can ignore the third term in Eq 22 yielding

\[
F[n] = k_B T \int d^3 r n(r) \left( \ln \left( \frac{n(r) \lambda^3}{2} \right) - 1 \right), \tag{23}
\]

where \(\lambda = (2\pi / k_B T)^{1/2}\) is the thermal de Broglie wavelength. Eq. 23 is identical to the Helmholtz free energy functional of the ideal classical gas, apart from the residual spin degeneracy factor \((2s + 1)\). Employing Eq. 23 from the outset corresponds to implementing the classical DFT [43]–[44] that generates PB theory for the one-component plasma. In the classical limit the TF screening length \(\lambda_{TF}\) [45], reduces to the Debye length \(\lambda_D\) of the OCP, given by \((\lambda_D)^{-2} = 4\pi e^2 n / k_B T\).

In Fig. 5 we show relative errors as a function of \(t = T/T_F\) over a larger temperature range than Fig. 1 (c). The blue KS approximation (blue curve) performs well across the range. Blue TF (purple curve) overestimates the XC free energy up to \(t \approx 10\); for larger values, all results merge. The classical approximation (green curve) becomes exact at sufficiently high \(t\).

In the classical limit (Boltzmann statistics) the CP approach is equivalent to the Percus test particle procedure [33]–[46]. Fixing a (classical) particle at the origin constitutes an external potential for the others. The resulting one-body density is proportional to the pair correlation function of the liquid [47]. The Percus procedure for quantum systems was pioneered by Chihara [46] and the most successful applications relate to liquid metals and electron correlations [48].

![FIG. 5. Percentage error of uniform gas potential XC free energy per electron for the CP-DFT calculations within KS (blue), TF (purple), and classical (green) approximations relative to the parameterization of Karasiev et al. [10]. See Fig. 1 (c) for additional context.](image)

In conclusion, CP DFT is formally exact, practical, and with a simple approximation, overcomes some limitations of KS DFT. The blue-electron approximation becomes exact in many limits: large separations, classical particles, and high temperatures. It may be exact even for strictly correlated electrons, where

\[
\tilde{n}_j^3(r') = \sum_{j=1}^{N-1} \delta^{(3)}(r' - f_j(r)), \tag{24}
\]

and \(f_j(r)\) is a co-location function [49]. Several longer works will follow.

R.J.M. supported by University of California President’s Postdoctoral Fellowship, K.B. and D.P. by DOE DE-FG02-08ER46496, R.P. and S.R.W. by DOE de-sc0008690, and R.E. by Leverhulme Trust EM 2020-029/4. K.B. thanks John Perdew for suggesting a variation on this in 1993.

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