Lattice density-functional theory for quantum chemistry

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We propose a lattice density-functional theory for *ab initio* quantum chemistry or physics as a route to an efficient approach that approximates the full configuration interaction energy and orbital occupations for molecules with strongly correlated electrons. We build on lattice density-functional theory for the Hubbard model by deriving Kohn-Sham equations for a reduced then full quantum chemistry Hamiltonian and demonstrate the method on the potential energy curves for the challenging problem of modeling elongating bonds in a linear chain of six hydrogen atoms. Here the accuracy of the Bethe-ansatz local-density approximation is tested for this quantum chemistry system, and we find that, despite this approximate functional being designed for the Hubbard model, the shapes of the potential curves generally agree with the full configuration interaction results. Although there is a discrepancy for very stretched bonds, it is lower than when using standard density-functional theory with the local-density approximation.

I. INTRODUCTION

Efficient computational methods based on small corrections to a single determinant of one-electron orbitals in *ab initio* quantum chemistry and physics can give qualitatively incorrect results if applied to electronically excited states, molecules containing transition metals, or bond breaking, for example, when elegant approximations in coupled-cluster theory are used to model the dissociation of the nitrogen dimer [1]. Such problems may require multiple determinants as the starting point of a now computationally intensive calculation and are often termed multireference or even strongly correlated. Full configuration interaction (FCI) gives the most accurate result for a given basis set of one-electron orbitals. However, as the number of determinants scales factorially with the size of the basis set, it is computationally prohibitive for all but the smallest systems. If there are K basis functions and $N_\uparrow + N_\downarrow$ electrons, then the FCI wave function will consist of $\binom{K}{N_\uparrow}\binom{K}{N_\downarrow}$ determinants when there are no symmetries to exploit. This means that for only 20 basis functions and 20 electrons with equal numbers of both spins, then there are already $\sim 10^{10}$ configurations, and finding their coefficients in the FCI wave function by diagonalization of the Hamiltonian matrix will be computationally intractable. By using the electron density rather than the many-electron wave function, density-functional theory (DFT) can, in principle, efficiently describe even strongly correlated systems. However, in practice standard approximate functionals can perform poorly when confronted with multireference problems, e.g., the dissociation of the hydrogen molecule [2] or spin gaps in transition-metal complexes [3].

Yet lattice DFT (LDFT) [4–6] with, e.g., the Bethe-ansatz local-density approximation (BA-LDA) [7] allows strongly correlated lattice systems, such as Hubbard models, to be

successfully and efficiently modeled [8] where the lattice density or site occupation takes the role of the density in standard DFT. Applications to Hubbard models have included modeling the system with periodic modulations in the external potential and on-site repulsion [9], using a harmonic potential to investigate the Luther-Emery phase [10], modeling ultracold repulsive fermions in one-dimensional optical lattices [11] and then simulating experimental data of cold atoms in optical lattices [12], and calculating the site entanglement when external potentials are used [13]. Accurate results for the local density and magnetization in spatially inhomogeneous spin-polarized systems have been obtained using an analytic parametrization for a Bethe-ansatz local-spin-density approximation [14]. An adiabatic BA-LDA for time-dependent LDFT has been created [15] and used to model the Coulomb blockade in quantum dots [16]. The μ-BA-LDA has been created, which uses the local chemical potentials to enable convergence in LDFT when site densities are close to 1 [17]. LDFT for the Hubbard model has been built upon with a one-electron reduced density matrix functional for the interaction energy [18], and the iBA-LDA was developed [19] for site-occupation embedding theory. The accuracy of approximations in LDFT has also been appraised using metric space approaches [20]. Similar to the Hohenberg-Kohn theorems [21] providing the foundation of standard DFT, LDFT depends on the result that the site density uniquely determines the wave function [22–24], and it was recently proven that for lattice systems, with certain caveats, the wave function uniquely determines the external potential [25].

The quantum chemistry Hamiltonian in a basis set of single-particle orbitals may be mapped to a lattice system where sites represent orbitals when using the notation of second quantization, which the Hubbard model approximates. This has enabled the impressive use of the powerful approach of the density matrix renormalization group (DMRG) [26] for multireference problems in quantum chemistry [27]. A DMRG calculation is systematically improvable by increasing

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the number of states (M), is variational, and can be successful for molecules that are beyond other wave function methods [28]. However, the accuracy can depend on the orbital ordering when mapped to a lattice system, and for K basis orbitals the scaling [27] of the calculation as $O(M^3 K^3) + O(M^2 K^4)$ means it can become computationally intractable as the system size increases if a large M is necessary for accurate results.

We also consider the quantum chemistry Hamiltonian mapped to a lattice system when using a basis set and use this to create a quantum chemistry lattice DFT (QC-LDFT) to approximate the FCI site density (orbital occupation) and energy as an essential step towards an efficient approach to model multireference problems in quantum chemistry. Although the accuracy will depend on the choice of approximate functional, only site densities from self-consistently solving a noninteracting system are required, rather than a many-electron wave function for the interacting system. This means that for K basis orbitals one has to diagonalize only $K \times K$ symmetric matrices, thereby incurring a computational cost that scales as $O(K^3)$ [29].

In this paper we first briefly discuss LDFT and the BA-LDA for the Hubbard model. Next, we derive the equations for QC-LDFT for which we consider a reduced Hamiltonian with interaction terms limited to those involving intersite densities before considering the full quantum chemistry Hamiltonian. The numerical procedures we employ to implement QC-LDFT are then presented. We then go beyond the Hubbard model and demonstrate QC-LDFT on the potential energy curve for a linear chain of six hydrogens when using 12 basis functions, where we test the accuracy of the BA-LDA functional [7]. We first use the reduced Hamiltonian before considering the full quantum chemistry Hamiltonian for this initial application of QC-LDFT. Despite using an approximate functional designed for the Hubbard model (the BA-LDA) [7], we capture the shapes of the FCI potential curves and, for the full Hamiltonian, improve upon standard DFT results at stretched bond lengths.

II. METHODS

A. Lattice density-functional theory

LDFT allows the efficient modeling of the Hubbard model when inhomogeneity is introduced through an external potential $v_{\text{ext},i}$. The Hamiltonian of this interacting system is

$$\hat{H}_{HM} = -t \sum_{i,\sigma} (\hat{a}_{i,\sigma}^\dagger \hat{a}_{i+1,\sigma} + \hat{a}_{i+1,\sigma}^\dagger \hat{a}_{i,\sigma})$$
$$+ U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} + \sum_i v_{\text{ext},i} \hat{n}_i, \quad (1)$$

where $\hat{a}_{i,\sigma}^\dagger$ creates a particle of spin σ at site i, while $\hat{a}_{i,\sigma}$ annihilates it, and the number operator or site density operator is $\hat{n}_{i,\sigma} = \hat{a}_{i,\sigma}^\dagger \hat{a}_{i,\sigma}$.

In the Kohn-Sham (KS) [30] approach to LDFT (see, e.g., Ref. [8]), the exact energy is written as a functional of the site density or occupation,

$$E[n] = T_{NI}[n] + E_H[n] + \sum_i v_{\text{ext},i} n_i + E_{xc}[n], \quad (2)$$

where T_{NI} is labeled the kinetic energy term for noninteracting electrons, E_H is the Hartree term, and E_{xc} is the exchange-correlation energy functional. As the exact form for this latter quantity is unknown, approximations have to be used in practice, and therefore the energy is approximate. The site density or occupation n_i is then found by self-consistently solving the noninteracting KS Hamiltonian

$$\hat{H}_{KS} = \hat{T} + \sum_i v_{\text{eff},i}[n] \hat{n}_i, \quad (3)$$

where $\hat{T} = -t \sum_{i,\sigma} (\hat{a}_{i,\sigma}^\dagger \hat{a}_{i+1,\sigma} + \hat{a}_{i+1,\sigma}^\dagger \hat{a}_{i,\sigma})$ is labeled the kinetic energy operator for the Hubbard model and

$$v_{\text{eff},i}[n] = \frac{\partial E_H}{\partial n_i} + v_{\text{ext},i} + \frac{\partial E_{xc}}{\partial n_i}$$
$$= v_{H,i}[n] + v_{\text{ext},i} + v_{xc,i}[n]. \quad (4)$$

For N electrons when the spins are balanced, the first $N/2$ eigenfunctions f_j form the single Slater determinant, which gives the site density as $n = 2 \sum_j^{N/2} |f_j|^2$, and $T_{NI} = 2 \sum_j^{N/2} \langle f_j | \hat{T} | f_j \rangle$, allowing $E[n]$ to be computed. We emphasize that although the occupation of f_j cannot be fractional, as these are the Kohn-Sham orbitals, the density or occupation at a site is a continuous variable that would be identical to that of the interacting system if the exact exchange-correlation potential v_{xc} were known.

B. Bethe-Ansatz local-density approximation

A LDA using the Bethe ansatz was first introduced for LDFT in Ref. [22]; later, the BA-LDA [7] became a popular and successful approximation to E_{xc} in LDFT. The BA-LDA interpolates three limiting cases ($U \to \infty$ with $n \leqslant 1$, $U = 0$ with $n \leqslant 1$, and $n = 1$) of the exact Bethe-ansatz energy results for the homogeneous Hubbard model, i.e., Eq. (1) when $v_{\text{ext}} = 0$. The interpolation uses [7]

$$e(n, t, U) = -\frac{2t\beta(U/t)}{\pi} \sin\left(\frac{\pi n}{\beta(U/t)}\right) \quad (5)$$

as the functional form for the energy per site when $n \leqslant 1$. Here $\beta(U/t)$ is found by using a Newton-Raphson procedure, so that the three limits are satisfied. The exchange-correlation functional for the BA-LDA [7] is

$$E_{xc}^{\text{BA-LDA}} = \sum_i e_{xc}(n_i, t, U), \quad (6)$$

where, analogously to standard DFT, a local functional is created by subtracting the per site noninteracting kinetic energy and Hartree energy for the homogeneous Hubbard model,

$$e_{xc}(n_i, t, U) = e(n_i, t, U) - e(n_i, t, 0) - e_H(n_i, U)$$
$$= -\frac{2t\beta(U/t)}{\pi} \sin\left(\frac{\pi n}{\beta(U/t)}\right)$$
$$+ \frac{4t}{\pi} \sin\left(\frac{\pi n_i}{2}\right) - \frac{U n_i^2}{4}. \quad (7)$$

Other choices for $e_H(n_i, U)$ are possible, but this one is often employed by considering that for balanced spins $\langle \hat{n}_{i,\sigma} \rangle = n_i/2$ [8]. For $n_i > 1$ the particle-hole transformation for the Hubbard model gives $e(n_i > 1, t, U) = e(2 - n_i, t, U) +$

$U(n_i - 1)$, which for all n_i values can be succinctly accounted for by using $e_{xc}(1 - |n_i - 1|, t, U)$ [31]. This means that $v_{xc}^{\mathrm{BA-LDA}}(n_i > 1, t, U) = -v_{xc}^{\mathrm{BA-LDA}}(2 - n_i, t, U)$, and there is a discontinuity at $n_i = 1$ which, as noted in Ref. [31], can cause convergence issues when self-consistently solving the KS equation in this case.

C. Quantum chemistry lattice density-functional theory

For an orthonormal basis set of single-particle orbitals, the quantum chemistry Hamiltonian can be written as a lattice Hamiltonian using the notation of second quantization [32] as

$$\hat{H} = \sum_{pq\sigma} h_{pq}\hat{a}_{p\sigma}^{\dagger}\hat{a}_{q\sigma} + \frac{1}{2}\sum_{pqrs\sigma\sigma'}\langle pr|qs\rangle\hat{a}_{p\sigma}^{\dagger}\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{q\sigma}, \quad (8)$$

and it is this mapping that allows the powerful approach of DMRG to be used for quantum chemistry. As orbitals are mapped to sites, if we can calculate the exact site occupation then we will find the orbital occupation for the FCI wave function. Here σ and σ' label the spins, h_{pq} are the one-electron integrals for spatial orbitals ϕ_p and ϕ_q, while the two-electron integrals are

$$\langle pr|qs\rangle = \iint \frac{\phi_p^*(\vec{r}_1)\phi_r^*(\vec{r}_2)\phi_q(\vec{r}_1)\phi_s(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d\vec{r}_1 d\vec{r}_2, \quad (9)$$

and atomic units are used. For K basis functions, the number of two-electron integrals will scale as $O(K^4)$, but the evaluation of them for Gaussian basis sets is fast, so this would become a bottleneck only for very large basis sets. In this case, by localizing orbitals, approximations could be employed to consider only near orbitals and reduce the severity of this scaling.

To create QC-LDFT we make Eq. (8) amenable to the construction of a LDFT KS equation by using the fermionic anticommutation relations $\{\hat{a}_{i\sigma}, \hat{a}_{j\sigma'}\} = 0$, $\{\hat{a}_{i\sigma}^{\dagger}, \hat{a}_{j\sigma'}^{\dagger}\} = 0$, and $\{\hat{a}_{i\sigma}^{\dagger}, \hat{a}_{j\sigma'}\} = \delta_{ij}\delta_{\sigma\sigma'}$ to give terms involving the site density (orbital occupation) operator $\hat{n}_i = \hat{a}_i^{\dagger}\hat{a}_i$.

1. Reduced Hamiltonian

We first consider the two-electron terms $\langle pp|pp\rangle$ and $\sigma \neq \sigma'$ which would correspond to on-site repulsion in the Hubbard model if all $\langle pp|pp\rangle$ were set to U. Using the anticommutation relations, we have $\hat{a}_{p\sigma}^{\dagger}\hat{a}_{p\sigma'}^{\dagger}\hat{a}_{p\sigma'}\hat{a}_{p\sigma} = -\hat{a}_{p\sigma}^{\dagger}\hat{a}_{p\sigma'}^{\dagger}\hat{a}_{p\sigma}\hat{a}_{p\sigma'} = \hat{a}_{p\sigma}^{\dagger}\hat{a}_{p\sigma}\hat{a}_{p\sigma'}^{\dagger}\hat{a}_{p\sigma'} = \hat{n}_{p\sigma}\hat{n}_{p\sigma'}$. This means that the terms in the Hamiltonian can be written as $\frac{1}{2}\sum_{p\sigma\sigma'}\langle pp|pp\rangle\hat{n}_{p\sigma}\hat{n}_{p\sigma'}$, which becomes $\frac{1}{2}\sum_p\langle pp|pp\rangle(\hat{n}_{p\uparrow}\hat{n}_{p\downarrow} + \hat{n}_{p\downarrow}\hat{n}_{p\uparrow})$ when summing over spins.

We then employ the approach from LDFT [8] of using $\langle\hat{n}_{i,\sigma}\rangle = n_i/2$ when the spins are balanced to give

$$E_H = \frac{1}{4}\sum_p\langle pp|pp\rangle n_p^2. \quad (10)$$

The contribution to $v_{\mathrm{eff},i}$ in the KS equation is then

$$v_{H,i} = \frac{\partial E_H}{\partial n_i} = \frac{1}{2}\langle ii|ii\rangle n_i. \quad (11)$$

For clarity we note that n_i, the site density or occupation, is the orbital occupation for the basis of orbitals that were

mapped to the sites in the lattice Hamiltonian [Eq. (8)]. It is not the occupation of the eigenfunctions of the KS LDFT Hamiltonian in its single-determinant wave function as, by construction, their occupation cannot be fractional.

We next have the $\langle pr|pr\rangle$ terms where $r \neq p$ and the anticommutation relations now lead to $\frac{1}{2}\sum_{p,r,(p\neq r)\sigma\sigma'}\langle pr|pr\rangle\hat{n}_{p\sigma}\hat{n}_{r\sigma'}$. Using $\langle\hat{n}_{i,\sigma}\rangle = n_i/2$ and the fact that there are four spin combinations gives another energy contribution in terms of the density that we denote as the second Hartree term (H2),

$$E_{H2} = \frac{1}{2}\sum_{p,r,(p\neq r)}\langle pr|pr\rangle n_p n_r, \quad (12)$$

resulting in another contribution to $v_{\mathrm{eff},i}$ of

$$v_{H2,i} = \frac{\partial E_{H2}}{\partial n_i} = \sum_{r,(r\neq i)}\langle ir|ir\rangle n_r, \quad (13)$$

where we have used that $\langle ir|ir\rangle = \langle ri|ri\rangle$.

At this point we can write a KS LDFT equation for a reduced quantum chemistry Hamiltonian where two-electron integrals beyond $\langle pp|pp\rangle$ and $\langle pr|pr\rangle$ are neglected,

$$\hat{H}_{\mathrm{red,KS}} = \sum_{p,q,(p\neq q)}h_{pq}\hat{a}_p^{\dagger}\hat{a}_q$$
$$+ \sum_i(v_{\mathrm{ext},i} + v_{H,i} + v_{H2,i} + v_{xc,i})\hat{n}_i. \quad (14)$$

Here the first term is $\hat{T}$, while $v_{\mathrm{ext},i} = h_{ii}$, $v_{H,i} = \frac{1}{2}\langle ii|ii\rangle n_i$, and $v_{H2,i} = \sum_{r,(r\neq i)}\langle ir|ir\rangle n_r$.

2. Full Hamiltonian

We now consider terms of the form $\langle pr|ps\rangle$ where $r \neq s$ and the anticommutation relations give $\hat{a}_{p\sigma}^{\dagger}\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{p\sigma} = -\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{p\sigma}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{p\sigma} = \hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{p\sigma}^{\dagger}\hat{a}_{p\sigma} - \hat{a}_{r\sigma'}^{\dagger}\delta_{sp}\delta_{\sigma\sigma'}\hat{a}_{p\sigma}$. So for the contribution to the quantum chemistry Hamiltonian we have

$$\frac{1}{2}\sum_{p,r,s,(r\neq s),\sigma\sigma'}\langle pr|ps\rangle\hat{a}_{p\sigma}^{\dagger}\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{p\sigma}$$
$$= \frac{1}{2}\sum_{p,r,s,(r\neq s),\sigma\sigma'}\langle pr|ps\rangle\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{n}_{p\sigma}$$
$$- \frac{1}{2}\sum_{r,s,(r\neq s),\sigma}\langle sr|ss\rangle\hat{a}_{r\sigma}^{\dagger}\hat{a}_{s\sigma}. \quad (15)$$

This does not have an expression in terms of only the site density, but when the spins are balanced, we again use $\langle\hat{n}_{i,\sigma}\rangle = n_i/2$ to give the contribution to the KS equation. We take into account the sum over spins for the site density to give $\frac{1}{2}\sum_{p,r,s,(r\neq s)}\langle pr|ps\rangle\hat{a}_r^{\dagger}\hat{a}_s n_p - \frac{1}{2}\sum_{r,s,(r\neq s)}\langle sr|ss\rangle\hat{a}_r^{\dagger}\hat{a}_s$, which due to the occurrence of $\hat{a}_p^{\dagger}\hat{a}_q$ terms becomes an addition to $\hat{T}$ in the KS equation.

A similar procedure for the contribution of $\langle pr|qr\rangle$ where $p \neq q$ results in the terms $\frac{1}{2}\sum_{p,q,r,(p\neq q)}\langle pr|qr\rangle\hat{a}_p^{\dagger}\hat{a}_q n_r - \frac{1}{2}\sum_{p,q,(p\neq q)}\langle pq|qq\rangle\hat{a}_p^{\dagger}\hat{a}_q$ being included in the KS Hamiltonian as an addition to $\hat{T}$.

Finally, the only remaining integrals to consider are $\langle pr|qs \rangle$ where $p \neq q$ and $r \neq s$. After rearranging the creation and annihilation operators we have $\hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma} \hat{a}_{r\sigma'}^\dagger \hat{a}_{s\sigma'} - \hat{a}_{p\sigma}^\dagger \delta_{rq} \delta_{\sigma\sigma'} \hat{a}_{s\sigma'}$. The first term cannot be rewritten using the site density and is a pure two-electron term, so it does not occur in the KS equation. This leaves $-\frac{1}{2} \sum_{p,q,s,(p\neq q,q\neq s)} \langle pq|qs \rangle \hat{a}_p^\dagger \hat{a}_s$ as the addition to $\hat{T}$ when $p \neq s$ and to v_{eff} when $p = s$.

Combining these results with the reduced KS Hamiltonian [Eq. (14)] gives the full KS Hamiltonian for QC-LDFT,

$$\hat{H}_{\text{full,KS}} = \hat{T} + \sum_i v_{\text{eff},i} \hat{n}_i, \tag{16}$$

where

$$\begin{aligned}
\hat{T} = {} & \sum_{p,q,(p\neq q)} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{p,r,s,(r\neq s)} \langle pr|ps \rangle \hat{a}_r^\dagger \hat{a}_s n_p \\
& - \frac{1}{2} \sum_{r,s,(r\neq s)} \langle rr|rs \rangle \hat{a}_r^\dagger \hat{a}_s + \frac{1}{2} \sum_{p,q,r,(p\neq q)} \langle pr|qr \rangle \hat{a}_p^\dagger \hat{a}_q n_r \\
& - \frac{1}{2} \sum_{p,q,(p\neq q)} \langle pq|qq \rangle \hat{a}_p^\dagger \hat{a}_q \\
& - \frac{1}{2} \sum_{p,q,s,(p\neq q,q\neq s,p\neq s)} \langle pq|qs \rangle \hat{a}_p^\dagger \hat{a}_s \tag{17}
\end{aligned}$$

and

$$v_{\text{eff},i} = v_{\text{ext},i} + v_{H,i} + v_{H2,i} + v_{H3,i} + v_{xc,i}. \tag{18}$$

Here the contributions to $v_{\text{eff},i}$ are the same as for the reduced Hamiltonian [Eq. (14)] except there is now a third Hartree potential,

$$v_{H3,i} = -\frac{1}{2} \sum_{q,(q\neq i)} \langle iq|qi \rangle. \tag{19}$$

D. Numerical procedure

For the BA-LDA in QC-LDFT we use $e_{xc}(n_i, t_i, U_i)$ in the approximation for E_{xc} [Eq. (6)] as approximate U and t values are now site dependent. Through comparison of the quantum chemistry Hamiltonian [Eq. (8)] with that of the Hubbard model [Eq. (1)] we see that $U_i = \langle ii|ii \rangle$ and take the average of the one-electron "hopping" integrals to calculate t_i values,

$$t_i = -\frac{1}{2}(h_{i,i+1} + h_{i-1,i}). \tag{20}$$

We have periodic boundary conditions as all orbitals can, in principle, interact, so that for K orbitals $t_K = -\frac{1}{2}(h_{K,1} + h_{K-1,K})$ and $t_1 = -\frac{1}{2}(h_{1,2} + h_{K,1})$. We generate the one-electron and two-electron quantum chemistry integrals using the program MOLPRO [33].

As the BA-LDA is exact for three limiting cases of the homogeneous Hubbard model, it would be expected to work best when site densities or occupations are not too different from one another. In this case if substantially more orbitals are used than electrons, then the chance that some n_i are close to 1 is also reduced. Furthermore, we would like the t_i values to be non-negligible and similar because if some are close to zero, then the calculation of $\beta(U_i/t_i)$ in the BA-LDA expression for the energy per site [Eq. (5)] will become unreliable. To make it more likely that the t_i values are similar

and that the site densities or occupations are not too far from homogeneity, we do not use Hartree-Fock molecular orbitals but begin with K atomic orbitals and then orthogonalize them in a balanced way by using symmetric orthogonalization [34]. This transforms the nonorthogonal orbitals $\int \phi_r^* \phi_s = \Delta_{rs}$ to $\int \tilde{\phi}_u^* \tilde{\phi}_v = \delta_{uv}$ using $\tilde{\phi}_u = \sum_i \Delta_{iu}^{-\frac{1}{2}} \phi_i$.

With the aim of making the self-consistent calculations more robust and accelerating convergence we use a Newton-Raphson approach to solve

$$\vec{G}(\vec{n}) = \vec{O}(\vec{n}) - \vec{n} = 0. \tag{21}$$

Here $\vec{O}(\vec{n})$ is the site density from the KS eigenfunctions when the site density $\vec{n}$ is used in the KS equation. This gives the site density for iteration $i + 1$ as

$$\vec{n}(i+1) = \vec{n}(i) - \boldsymbol{J}^{-1}\vec{G}(\vec{n}(i)), \tag{22}$$

where $\boldsymbol{J}$ is the Jacobian matrix for $\vec{G}$. We calculate $\boldsymbol{J}$ numerically with a step size of 0.01 as solving the KS equation for given site densities is very fast. To also improve stability we implement density mixing where $\vec{n}(i+1)_{mix} = 0.2\vec{n}(i+1) + 0.8\vec{n}(i)$. From the fourth iteration we check the average difference between the input and output site densities for the KS equation, which we denote as the error:

$$\text{Error} = \frac{1}{K} \sum_{i=1}^{K} |O_i(\vec{n}) - n_i|. \tag{23}$$

We use a threshold of 10^{-7} for this to ascertain if convergence has been reached when solving the KS equation self-consistently.

III. RESULTS

We demonstrate QC-LDFT with the BA-LDA by calculating potential energy curves as the bond length is varied for a linear chain of six hydrogen atoms. The 3-21G basis set is employed, resulting in 12 single-particle orbitals. We use a default ordering for the orbitals in the lattice, so sites 1 and 2 represent the symmetrically orthogonalized atomic orbitals of the first hydrogen, sites 3 and 4 represent those of the second hydrogen, and so on.

First, we investigate the reduced Hamiltonian when two-electron integrals beyond $\langle pp|pp \rangle$ and $\langle pr|pr \rangle$ are neglected and its corresponding LDFT KS equation [Eq. (14)]. We see in Fig. 1 that a binding curve is recovered by the FCI results despite using a reduced Hamiltonian. This fits in with results [35] that a Hubbard model with intersite repulsion could have parameters derived to reasonably describe potential curves of the hydrogen molecule. The FCI and QC-LDFT potential curves are shifted in Fig. 1, so both have zero as their minimum, and we see that QC-LDFT reproduces the shape of the curve and is in good agreement with FCI except around bond lengths of 3 Å or longer where the QC-LDFT results are a little high.

We found that 48 400 determinants were needed for the FCI calculation, and due to the use of symmetric orthonormalization of the atomic orbitals even at the equilibrium bond length of 0.8 Å many determinants are important. We quantify this using an indicator [36,37] of the FCI wave function's
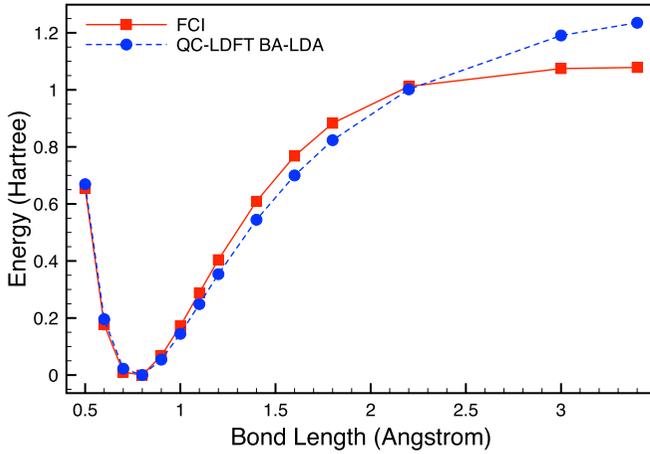
FIG. 1. Reduced Hamiltonian energy results from FCI and QC-LDFT with the BA-LDA for a linear chain of six hydrogens as the bond lengths are varied, using the 3-21G basis and shifting the potential curves so that both have their minimum at zero.

multireference character

$$MR = \sum_i |c_i|^2 - |c_i|^4, \qquad (24)$$

where c_i is the coefficient of determinant i and the wave function is normalized so that $\sum_i |c_i|^2 = 1$. MR is zero for a wave function consisting of a single determinant, while the value approaches 1 as the number of important determinants increases. Even at the equilibrium bond length we find MR = 0.9999, which demonstrates the very strong multireference character when using atomic orbitals with symmetric orthonormalization.

The full quantum chemistry Hamiltonian is now considered using FCI and QC-LDFT with the BA-LDA. For comparison, results from standard DFT with the LDA are calculated using MOLPRO [33]. We see in Fig. 2 that the general shape of
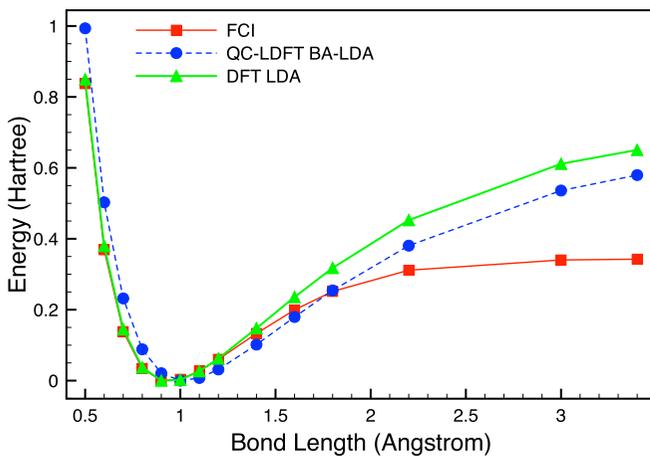
FIG. 2. Full Hamiltonian energy results from FCI, QC-LDFT with the BA-LDA, and standard DFT with the LDA for a linear chain of six hydrogens as the bond lengths are varied, using the 3-21G basis and shifting the potential curves so that all have their minimum at zero.
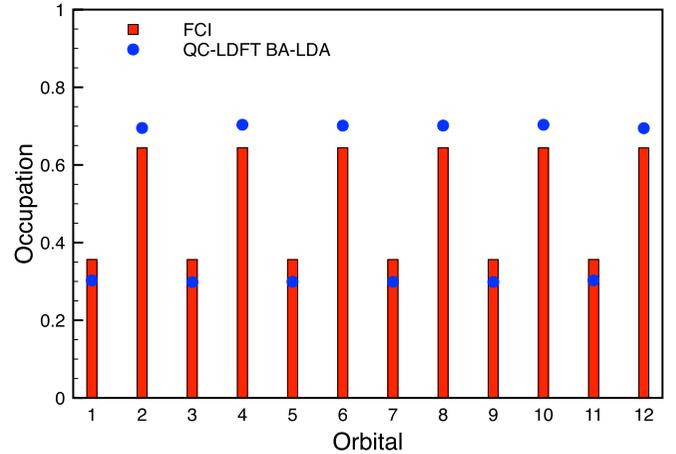
FIG. 3. Full Hamiltonian orbital occupancy results for FCI and QC-LDFT with the BA-LDA for a linear chain of six hydrogens at a bond length of 3.4 Å using the 3-21G basis.

the FCI binding curve is again captured by QC-LDFT, but the discrepancy at large bond lengths is more apparent.

We speculate that this is due to the BA-LDA being based on the Hubbard model, which means it does not include the one-electron integrals beyond nearest neighbors or the extra Hartree terms that occur in the quantum chemistry KS Hamiltonian [Eq. (18)]. This fits in with the difference with the exact result being less pronounced for the reduced Hamiltonian in Fig. 1 as there is only one additional Hartree term for the KS equation in this case [Eq. (14)]. The minimum energy is at 0.9 Å for both FCI and DFT, while QC-LDFT is close to this at 1.0 Å. The DFT results are closer to FCI at shorter bond lengths, but QC-LDFT performs better as the bonds are elongated.

We quantify the overall error in the potential curves compared with FCI using $\sigma_{\Delta E}$ from Refs. [20,38], where

$$\sigma_{\Delta E} = \sqrt{\frac{1}{d}\sum_{j=1}^{d}(\Delta E_j - \mu_{\Delta E})^2} \qquad (25)$$

is the standard deviation of the difference in energies $\Delta E_j = E_j^{\text{FCI}} - E_j^{\text{approx}}$ for all d points in the potential energy curve and $\mu_{\Delta E}$ is the mean value of ΔE. This takes into account all of the points and that the curves can be shifted by a constant. This gives 0.086 and 0.100 hartree for QC-LDFT and DFT, respectively, showing that for these points QC-LDFT is slightly more accurate by this measure. Again, the orbitals used mean that the problem is strongly multireference for FCI and QC-LDFT at all points considered. In addition the values for U_i/t_i are around 1 to 5 at both 1.0 and 3.4 Å. We see in Fig. 3 that at 3.4 Å, where there is a more noticeable difference between the FCI and QC-LDFT potential energy curves, the orbital occupations calculated using QC-LDFT are slightly different from the FCI results but have a very similar pattern. This suggests that a functional designed specifically for QC-LDFT should be able to correct the discrepancy in energies for this region.

IV. SUMMARY

We created a lattice density-functional theory for *ab initio* quantum chemistry or physics by considering the quantum chemistry Hamiltonian in the notation of second quantization where orbitals are mapped to sites on a lattice and deriving its LDFT Kohn-Sham equation. This represents an efficient approach to approximate the energy and orbital occupation of the full configuration interaction wave function as for K basis functions the cost of solving the LDFT Kohn-Sham equation then scales as $O(K^3)$. We demonstrated QC-LDFT on a linear chain of six hydrogen atoms with a basis set of 12 orbitals as the bond length was varied and tested the approximate BA-LDA [7] functional for this case. Remarkably, despite using this approximate functional designed for the Hubbard model, QC-LDFT captured the shape of the FCI potential energy curves for both reduced and full Hamiltonians. In the latter case a discrepancy was more noticeable at stretched bond lengths; however, there was an improvement over standard DFT here. Future work will consider optimizing the orbital ordering in the lattice, smoothing [39] of v_{xc} around $n = 1$, and going beyond the BA-LDA functional so that QC-LDFT can be applied successfully to more complex multireference or strongly correlated molecules.

[1] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[2] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008).

[3] M. Reiher, Inorg. Chem. **41**, 6928 (2002).

[4] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **56**, 1968 (1986).

[5] K. Schönhammer and O. Gunnarsson, J. Phys. C **20**, 3675 (1987).

[6] K. Schönhammer and O. Gunnarsson, Phys. Rev. B **37**, 3128 (1988).

[7] N. A. Lima, M. F. Silva, L. N. Oliveira, and K. Capelle, Phys. Rev. Lett. **90**, 146402 (2003).

[8] K. Capelle and V. L. Campo, Jr., Phys. Rep. **528**, 91 (2013).

[9] M. F. Silva, N. A. Lima, A. L. Malvezzi, and K. Capelle, Phys. Rev. B **71**, 125130 (2005).

[10] G. Xianlong, M. Rizzi, M. Polini, R. Fazio, M. P. Tosi, V. L. Campo, and K. Capelle, Phys. Rev. Lett. **98**, 030404 (2007).

[11] G. Xianlong, M. Polini, M. P. Tosi, V. L. Campo, K. Capelle, and M. Rigol, Phys. Rev. B **73**, 165120 (2006).

[12] V. L. Campo, K. Capelle, J. Quintanilla, and C. Hooley, Phys. Rev. Lett. **99**, 240403 (2007).

[13] V. V. França and K. Capelle, Phys. Rev. Lett. **100**, 070403 (2008).

[14] V. V. França, D. Vieira, and K. Capelle, New J. Phys. **14**, 073021 (2012).

[15] C. Verdozzi, Phys. Rev. Lett. **101**, 166401 (2008).

[16] S. Kurth, G. Stefanucci, E. Khosravi, C. Verdozzi, and E. K. U. Gross, Phys. Rev. Lett. **104**, 236801 (2010).

[17] Z.-J. Ying, V. Brosco, and J. Lorenzana, Phys. Rev. B **89**, 205130 (2014).

[18] M. Saubanère, M. B. Lepetit, and G. M. Pastor, Phys. Rev. B **94**, 045102 (2016).

[19] B. Senjean, N. Nakatani, M. Tsuchiizu, and E. Fromager, Phys. Rev. B **97**, 235105 (2018).

[20] V. V. França, J. P. Coe, and I. D'Amico, Sci. Rep. **8**, 664 (2018).

[21] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[22] K. Schönhammer, O. Gunnarsson, and R. M. Noack, Phys. Rev. B **52**, 2504 (1995).

[23] L.-A. Wu, M. S. Sarandy, D. A. Lidar, and L. J. Sham, Phys. Rev. A **74**, 052335 (2006).

[24] A. Schindlmayr and R. W. Godby, Phys. Rev. B **51**, 10427 (1995).

[25] J. P. Coe, I. D'Amico, and V. V. França, Europhys. Lett. **110**, 63001 (2015).

[26] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).

[27] G. K.-L. Chan and S. Sharma, Annu. Rev. Phys. Chem. **62**, 465 (2011).

[28] Y. Kurashige, G. K.-L. Chan, and T. Yanai, Nat. Chem. **5**, 660 (2013).

[29] J. W. Demmel, *Applied Numerical Linear Algebra* (Society for Industrial and Applied Mathematics, Philadelphia, 1997), pp. 212–213.

[30] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[31] A. Akande and S. Sanvito, Phys. Rev. B **82**, 245114 (2010).

[32] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).

[33] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2012.1, http://www.molpro.net.

[34] P.-O. Löwdin, Adv. Phys. **5**, 1 (1956).

[35] G. Chiappe, E. Louis, E. SanFabián, and J. A. Verges, Phys. Rev. B **75**, 195104 (2007).

[36] J. P. Coe, P. Murphy, and M. J. Paterson, Chem. Phys. Lett. **604**, 46 (2014).

[37] J. P. Coe and M. J. Paterson, J. Chem. Theory Comput. **11**, 4189 (2015).

[38] J. P. Coe and M. J. Paterson, J. Chem. Phys. **137**, 204108 (2012).

[39] D. Karlsson, A. Privitera, and C. Verdozzi, Phys. Rev. Lett. **106**, 116401 (2011).