

Variational grand-canonical electronic structure method for open systems

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An *ab initio* method is developed for variational grand-canonical molecular electronic structure of open systems based on the Gibbs–Peierls–Bogoliubov inequality. We describe the theory and a practical method for performing the calculations within standard quantum chemistry codes using Gaussian basis sets. The computational effort scales similarly to the ground-state Hartree–Fock method. The quality of the approximation is studied on a hydrogen molecule by comparing to the exact Gibbs free energy, computed using full configuration-interaction calculations. We find the approximation quite accurate, with errors similar to those of the Hartree–Fock method for ground-state (zero-temperature) calculations. A further demonstration is given of the temperature effects on the bending potential curve for water. Some future directions and applications of the method are discussed. Several appendices give the mathematical and algorithmic details of the method. © 2005 American Institute of Physics. [DOI: 10.1063/1.1949202]

I. INTRODUCTION

Electronic structure of open systems in contact with a heat and electron reservoirs is important in a variety of applications in chemistry, biology, solid state, nuclear, and laser physics as well as astronomy and materials science.^{1–21} Simulations, usually done using molecular dynamics (MD), typically assume an integer average number of electrons confined to their ground state. At high densities and temperatures this is often unjustified. Another case of interest is in embedding theories; where assuming a closed system leads to a slow convergence because of the need to considerably increase the size of the embedded cluster. The fact that very few studies allow for open system character is often due to lack of availability of reliable methods to compute electronic forces on nuclei in open system conditions.

This paper develops a theory analogous to the Hartree–Fock ground-state method,^{22,23} allowing a reliable variational calculation of the electronic structure for open systems. We consider a molecular system which is in thermodynamic equilibrium with a heat reservoir, characterized by a temperature $T=(k_B\beta)^{-1}$, where k_B is Boltzmann’s constant, and an electron reservoir, characterized by a chemical potential μ . As discussed below, the average force on nuclei in such systems is conservative, as it is when electrons are confined to their ground states (within the Born–Oppenheimer approximation), but the potential function is not the internal energy. Instead, it is the Gibbs free energy $G(\beta, \mu)$ through which all ensemble averages can be determined (in Sec. III B we explain this).

The *ab initio* method presented here yields a variational approximation to the Gibbs free energy we call the optimized effective free energy (OEFE). It can be straightforwardly applied using standard *ab initio* quantum-chemical codes. The

OEFE is of comparable quality to the Hartree–Fock energy for the electronic ground state. Both methods use an auxiliary noninteracting system for computing observables and energies. In that sense, we may say that the present method neglects electron correlation. This effect can be introduced into the framework we describe using correlation density functionals, as in the Kohn–Sham theory, which is valid for open systems in thermodynamical equilibrium.²⁴ Despite this lack of “correlation,” the attractive feature of the OEFE method is its variational weighting of *all* charged states and spin states. Thus, expensive excited-states methods are not needed here.

We discuss the OEFE theory in some detail and derive all results needed for an implementation using a standard quantum-chemical program. The formulation in terms of a grand-canonical ensemble greatly facilitates the derivations. It allows relatively simple and doable expressions for the various average quantities and gradients needed to minimize the OEFE. Issues, such as calculation of gradients, ensemble averages, and effective forces on nuclei, are all discussed at some length. Several appendices, carrying some of the more technical derivations, are given. We also discuss an extension of the method for computing an approximate Helmholtz free energy.

II. THE OPTIMIZED EFFECTIVE FIELD

The nonrelativistic Hamiltonian of electrons in a molecule can be generally written in atomic units as

$$\begin{aligned}
 H &= \sum_n \left[\frac{-\nabla_n^2}{2} + v_{\text{ext}}(\mathbf{r}_n) \right] - \sum_{n,A} \frac{Z_A}{r_{nA}} + \frac{1}{2} \sum_{n \neq m} \frac{1}{r_{nm}} \\
 &\equiv \hat{T} + \frac{1}{2} \sum_{n \neq m} \nu(r_{nm}),
 \end{aligned}
 \tag{2.1}$$

where lower and upper case indices are used to label coordinates of electrons and nuclei, respectively. \hat{T} is the one-body

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part of the Hamiltonian, including kinetic energy and interaction energy with external fields (v_{ext}) and the nuclei, while $u(r)=r^{-1}$ is the Coulomb repulsion potential between all pairs of electrons. We will use a second-quantized formulation in which all quantities are described with reference to an orthonormal basis of M real single-particle orbitals $\phi_i(\mathbf{r})$, $i=1,2,\dots,M$. The basic operators are the electron creation and annihilation operators. The operator \hat{c}_{js}^\dagger creates an electron of spin s (\uparrow or \downarrow) in orbital ϕ_j , while \hat{c}_{js} annihilates an electron in this same state. Because electrons are fermions, these operators have the well-known anticommutation relations²⁵ $[\hat{c}_{js}^\dagger, \hat{c}_{j's'}]_+ = \delta_{ss'} \delta_{jj'}$, $[\hat{c}_{js}, \hat{c}_{j's'}]_+ = [\hat{c}_{js}^\dagger, \hat{c}_{s't'}^\dagger]_+ = 0$. Using the creation and destruction operators, the Hamiltonian can be written as

$$\hat{H} = \sum_{ij,s} T_{ij} \hat{c}_{is}^\dagger \hat{c}_{js} + \frac{1}{2} \sum_{ijkl,s,s'} V_{ijkl} \hat{c}_{is}^\dagger \hat{c}_{ks'}^\dagger \hat{c}_{ls'} \hat{c}_{js}. \quad (2.2)$$

The parameters of the second-quantized Hamiltonian are then the ‘‘one-electron integrals,’’

$$T_{ij} = \int \phi_i(\mathbf{r}) \hat{T} \phi_j(\mathbf{r}) d^3r, \quad (2.3)$$

and the ‘‘two-electron integrals,’’

$$V_{ijkl} = \int \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) u(|\mathbf{r} - \mathbf{r}'|) \phi_k(\mathbf{r}') \phi_l(\mathbf{r}') d^3r d^3r'. \quad (2.4)$$

Since the matrices T and V of Eqs. (2.3) and (2.4) defining the interaction do not reference spin, it is thus useful to eliminate explicit reference to spin from the formalism. Let us then introduce the density-matrix operator with elements

$$\hat{\rho}_{ij} = \sum_{s=\uparrow\downarrow} \hat{c}_{is}^\dagger \hat{c}_{js}, \quad \hat{\rho}_{ij}^\dagger = \hat{\rho}_{ji}. \quad (2.5)$$

The Hamiltonian of Eq. (2.2) can then be written directly in terms of this density matrix as follows:

$$\hat{H} = \sum_{ij} t_{ij} \hat{\rho}_{ij} + \frac{1}{2} \sum_{ijkl} \hat{\rho}_{ij} V_{ijkl} \hat{\rho}_{kl}, \quad (2.6)$$

with

$$t_{ij} = T_{ij} - \frac{1}{2} \sum_l V_{ilkj}, \quad (2.7)$$

Next, we introduce a shorthand notation defining the composite index $I=(ij)$ [sometimes we will also write $K=(kl)$] and write the Hamiltonian of Eq. (2.6) in the following way:

$$\hat{H} = t^T \hat{\rho} + \frac{1}{2} \hat{\rho}^T V \rho. \quad (2.8)$$

Here, t and $\hat{\rho}$ are considered column vectors of dimension M^2 in the index I , respectively, consisting of the elements,

$$t_I = t_{ij}, \quad \hat{\rho}_I = \hat{\rho}_{ij}. \quad (2.9)$$

The $M^2 \times M^2$ matrix V elements are defined as

$$V_{IK} = V_{ijkl}, \quad (2.10)$$

and we use the mathematical notation,

$$A^T B = \sum_I A_I B_I. \quad (2.11)$$

A. The Gibbs free energy

The Gibbs free energy (henceforth, simply free energy) in the given basis²⁶ is

$$G(\beta, \mu) = -\beta^{-1} \ln Z(\beta, \mu), \quad (2.12)$$

where β is the inverse temperature, μ is the chemical potential, and $Z(\beta, \mu)$ is the partition function of the ensemble defined as

$$Z(\beta, \mu) = \sum_{N=0}^{2M} e^{\beta\mu N} \text{tr}_N[e^{-\beta\hat{H}}] = \text{tr}[e^{-\beta(\hat{H}-\mu\hat{N})}]. \quad (2.13)$$

The trace tr_N is over all antisymmetric N -electron states. The trace with no subscript is over all 2^{2M} antisymmetric states with *all possible number of electrons* (the second equality is valid for because \hat{H} conserves the number of electrons). Because of the Pauli principle, the maximal number of electrons is $2M$, since at most two electrons can be inserted into a single orbital. The ensemble average of an observable \hat{O} can be computed by

$$\langle \hat{O} \rangle_{\text{exact}} = Z^{-1} \text{tr}[e^{-\beta(\hat{H}-\mu\hat{N})} \hat{O}], \quad (2.14)$$

(the symbol $\langle \cdot \rangle_{\text{exact}}$ denotes an exact ensemble average in the interacting system, as opposed to averages for a noninteracting system, denoted $\langle \cdot \rangle$ as discussed below). In particular, the ensemble average number of particles $\hat{N} = \sum_{i=1}^M \hat{\rho}_{ii}$ is given by

$$\langle \hat{N} \rangle_{\text{exact}} = -\frac{\partial G}{\partial \mu}, \quad (2.15)$$

and the average energy is

$$\langle \hat{H} \rangle_{\text{exact}} = \frac{\partial(\beta G)}{\partial \beta} + \mu \langle \hat{N} \rangle_{\text{exact}}. \quad (2.16)$$

The second derivative of the free energy is proportional to the average fluctuation in the electron number,

$$\frac{\partial^2 G}{\partial \mu^2} = -\beta \langle (N - \langle N \rangle_{\text{exact}})^2 \rangle_{\text{exact}} \leq 0. \quad (2.17)$$

Since the fluctuation is always positive, we find from (2.15) and (2.17) that G as a function of μ is monotonic nonincreasing and convex upwards. Furthermore, $\langle N \rangle_{\text{exact}}$ is a monotonic nondecreasing function of μ . Similar considerations apply to βG as a function of β .

The physical meaning of G is in the work done on the electrons by external fields coupled through v_{ext} in Eq. (2.1). For example, suppose a nucleus is moved adiabatically (very slowly and at constants β and μ) in the molecule from a position \mathbf{R} to $\mathbf{R} + \delta\mathbf{R}$. The work that needs to be invested for this process is the scalar product of the average electronic force and the displacement,

$$\delta W = \left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle_{\text{exact}} \cdot \delta \mathbf{R}. \quad (2.18)$$

Using Eqs. (2.12)–(2.14), it is straightforward to verify the following relation:

$$-\left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle_{\text{exact}} = -\frac{\delta G}{\delta \mathbf{R}}. \quad (2.19)$$

Note, when taking the derivative, the fact that $\delta \hat{H} / \delta \mathbf{R}$ and \hat{H} are noncommutative is not an issue because the trace of a product of operators is invariant to cyclic permutations. We thus conclude that

$$\delta W = \frac{\delta G}{\delta \mathbf{R}} \cdot \delta \mathbf{R}, \quad (2.20)$$

showing that the average electronic force on the nuclei is a conservative field as it is the gradient of $-G$. The difference in free energy of two completely different nuclear configurations $\Delta G = G(\mathbf{R}_2) - G(\mathbf{R}_1)$ is therefore equal to the work that needs to be done on the electrons to adiabatically move the nuclei from \mathbf{R}_1 to \mathbf{R}_2 . This interpretation of the free energy as the work function is standard in thermodynamics. We use it below to give a definition of the grand-canonical averages that can be generalized to cases where only the approximate free energy is known.

B. The variational approximation

Because of the electron-electron interactions, calculating the grand-canonical partition function $Z(\beta, \mu)$ is practically impossible for any but the simplest model systems. However, if the electrons are noninteracting, there is a simple textbook solution. Let us introduce a noninteracting electron system with Hamiltonian,

$$\hat{H}_0 = h^T \hat{\rho} \equiv t^T \hat{\rho} + u^T \hat{\rho}, \quad (2.21)$$

where \hat{H}_0 is composed of the same one-body term as \hat{H} in Eq. (2.8), but there is an additional one-body field U . If the matrix $h = t + u$ has eigenvalues $\varepsilon_1, \varepsilon_2, \dots$, then the grand-canonical partition function [Eq. (2.13) with \hat{H} replaced by \hat{H}_0] is simply the Fermi–Dirac product function,²⁵

$$Z_0(\beta, \mu) = \prod_{l=1}^M (1 + e^{\beta(\mu - \varepsilon_l)})^2, \quad (2.22)$$

where the square of each term is a result of the maximal double occupancy of each state as dictated by the Pauli principle. This simple expression can be written in a compact form as^{17,27,28}

$$Z_0(\beta, \mu) = \det[1 + e^{\beta(\mu - h)}]^2. \quad (2.23)$$

Such a formula is extremely useful because computing the determinant and exponential of a matrix, as in Eq. (2.23), is considerably more economical than summing over 2^{2M} terms, as suggested in Eq. (2.13). Using the determinant form, the ensemble averages of one-, two- and three-particle operators are tractable, as shown below. It should be noted that the grand-canonical trace automatically sums over all

spin states and charged states of the molecule (here we use the term *molecule* in a wider than usual sense; by it we mean all ionic electronic states for the same nuclear configuration). Note also that evaluating a *canonical* ensemble partition function $Q(\beta, N) = \text{tr}_N e^{-\beta H_0}$ is actually more demanding than evaluating the grand partition function. The latter step involves $O(M^3)$ operations; the canonical trace sums over all N -electron states, which for a basis of $2M$ spin orbitals involves $\binom{2M}{N}$ operations. Nevertheless, many interesting problems involve a system which has a well-defined electron number, but is coupled to a heat reservoir. In this case, it may be advantageous to obtain the canonical energy from the grand-canonical free energy, as discussed in Appendix A.

Since noninteracting fermions are easily handled, it is natural to ask how to approximate the interacting system by a noninteracting one? One simple-minded approach would be to have u relate to V through

$$\langle \hat{H} - \hat{H}_0 \rangle = 0 \rightarrow \frac{1}{2} V_{JK} \langle \hat{\rho}_J \hat{\rho}_K \rangle - u_J \langle \hat{\rho}_J \rangle = 0. \quad (2.24)$$

Here and henceforth, the angular brackets $\langle \cdot \rangle$ are used to denote average with respect to \hat{H}_0 [in contrast with $\langle \cdot \rangle_{\text{exact}}$ in Eq. (2.14) for \hat{H}],

$$\langle \hat{O} \rangle = Z_0^{-1} \text{tr}[e^{-\beta(\hat{H}_0 - \mu \hat{N})} \hat{O}], \quad (2.25)$$

where $Z_0 = \text{tr}[e^{-\beta(\hat{H}_0 - \mu \hat{N})}]$. Equation (2.24) is a problematic approach. For one thing, the number of solutions is infinite; which one shall we use? Furthermore, it is desirable to search for some form of an *optimized* approximation.

Thus we go in a different route, invoking the Gibbs–Peierls–Bogoliubov inequality^{29–32} yielding an upper bound approximation, denoted Γ , for G ,

$$G(\beta, \mu) \leq \Gamma(\beta, \mu) \equiv G_0(\beta, \mu) + \langle \hat{H} - \hat{H}_0 \rangle, \quad (2.26)$$

where $G_0 = -\beta^{-1} \ln Z_0$ is the free energy of the noninteracting electron system. The new quantity $\Gamma(\beta, \mu)$ is called henceforth the *effective free energy*. By varying h (or equivalently u) in \hat{H}_0 , we can minimize $\Gamma(\beta, \mu)$ thus finding the *optimized effective Hamiltonian* $\hat{H}_0 = h^T \hat{\rho}$ and the corresponding OEFE Γ —the best variational approximation to $G(\beta, \mu)$. Once h is determined, u is defined and is called the *optimized effective field*, allowing for the two-body interaction V_{IJ} in \hat{H} .

III. THE OPTIMIZED EFFECTIVE FREE ENERGY

A. Determination of the optimized effective field

We now turn to the practical issue of how to actually calculate the optimized effective Hamiltonian h . Since t is known, it is more convenient to work in terms of the field $u = h - t$. Thus we search for the field minimizing the effective free energy,

$$\Gamma[u] = G_0[u] + \left\langle \frac{1}{2} \hat{\rho}^T V \hat{\rho} - u^T \hat{\rho} \right\rangle. \quad (3.1)$$

The first step is to compute the gradient of Γ with respect to a field matrix element $u_j \equiv u_{ij}$. It is shown in Appendix B that such a derivative results in the following expression:

$$\frac{\delta\Gamma}{\delta u_I} = \frac{1}{2}\beta V_{JK}[\langle\hat{\rho}_I\rangle\langle\hat{\rho}_J\hat{\rho}_K\rangle - \langle\bar{\rho}_I\hat{\rho}_J\hat{\rho}_K\rangle] - \beta u_{JL}[\langle\hat{\rho}_I\rangle\langle\hat{\rho}_J\rangle - \langle\bar{\rho}_I\hat{\rho}_J\rangle]. \quad (3.2)$$

Here and below we use the convention that repeated double indices are summed over. The operator $\bar{\rho}_I$ is a β -averaged density matrix given in Eq. (B3). The actual evaluation of the correlated averages appearing in Eq. (3.2) is discussed in Appendix C and the method of evaluating the various matrices is discussed in detail in Appendix D.

We write Eq. (3.2) in the equivalent, but more instructive form as follows:

$$\frac{\delta\Gamma}{\delta u_I} = \beta(\langle\hat{\rho}_I\rangle\langle\hat{H} - \hat{H}_0\rangle - \langle\hat{\rho}_I(\hat{H} - \hat{H}_0)\rangle). \quad (3.3)$$

At the minimum the following condition is met:

$$\frac{\delta\Gamma}{\delta u} = 0. \quad (3.4)$$

Thus, using Eq. (3.3), the optimized field is determined from the following set of equations (to be satisfied for each I):

$$\langle\hat{\rho}_I\rangle\langle\hat{H} - \hat{H}_0\rangle = \langle\hat{\rho}_I(\hat{H} - \hat{H}_0)\rangle. \quad (3.5)$$

Note that under the noninteracting ensemble, *any one-body operator* $O_I\hat{\rho}_I$ which commutes with the optimized \hat{H}_0 is statistically uncorrelated with the energy difference operator $\hat{H} - \hat{H}_0$. This is an immediate consequence of the fact that in this case $\bar{O} = \hat{O}$ [see Eq. (B3)]. In particular, we have for the number of electrons \hat{N} and \hat{H}_0 itself,

$$\langle\hat{N}(\hat{H} - \hat{H}_0)\rangle = \langle\hat{N}\rangle\langle\hat{H} - \hat{H}_0\rangle, \quad (3.6)$$

$$\langle\hat{H}_0(\hat{H} - \hat{H}_0)\rangle = \langle\hat{H}_0\rangle\langle\hat{H} - \hat{H}_0\rangle. \quad (3.7)$$

In deriving the above results, we have here introduced u as a convenience. We could have used h as the variational field. This would make no essential difference and, in fact, since h is directly determined by u , the following relation holds, in addition to Eq. (3.4):

$$\frac{\delta\Gamma}{\delta h} = 0. \quad (3.8)$$

At low temperatures ($\beta \rightarrow \infty$) and for a value of μ that yields an integer average electron number N , h becomes equal (up to a constant) to the Hartree–Fock matrix (the “Fockian”) and u becomes equal to the matrix of the direct (“Hartree”) and exchange (“Fock”) operators. This is because when $\beta \rightarrow \infty$ the ground-state Slater determinant(s) Ψ_0 of \hat{H}_0 dominates the partition function trace. Thus the optimal h must yield the determinant that lowers the expectation value of \hat{H} to its minimum, i.e., the Hartree–Fock determinant. The relation between the optimized effective free energy and the Hartree–Fock energy becomes in this limit,

$$\Gamma[u] + \mu N \xrightarrow{\beta \rightarrow \infty} \langle\Psi_0|t^T\hat{\rho} + \frac{1}{2}\hat{\rho}^T V\hat{\rho}|\Psi_0\rangle. \quad (3.9)$$

Yet, at higher than zero temperatures, the method departs from the Hartree–Fock method.

The overall complexity of the method is $O(M^4)$. In this paper we developed the method in a orthonormal basis, so there is an additional $O(M^5)$ step to transform the two-electron integrals. However, a similar theory within the atomic basis can be developed which scales as $O(M^4)$, i.e., the same complexity of the Hartree–Fock method within a similar basis set. This is attractive, given that the present method treats all excited states and multiplies charged states in a variational way.

B. Effective ensemble averages

What is the consistent way of evaluating expectation values in the variational approximation? This is not a trivial issue. For example, which is a more consistent way of evaluating the average number of electrons $\langle\hat{N}\rangle$? Is it

$$\frac{1}{Z_0}\text{tr}[e^{-\beta(\hat{H}_0 - \mu\hat{N})}\hat{N}] \quad \text{or} \quad -\frac{\delta\Gamma}{\delta\mu}? \quad (3.10)$$

The left option is the average value of the number operator in the noninteracting system. The right option is the analog of the exact relation given in Eq. (2.15).

The way we approach this question is by making a connection between average values and the free energy. Once such a connection is made, we can use the variational approximation to compute averages. For this purpose, note that the exact expectation value of an arbitrary operator \hat{O} , given in Eq. (2.14), can be interpreted in terms of work as follows. Let us introduce an external field s which couples to the electronic system through the n -body operator \hat{O} . Under a given value of the field, the free energy is

$$\tilde{G}(\beta, \mu, s) = -\beta^{-1} \ln \text{tr}[e^{-\beta[\hat{H} + s\hat{O} - \mu\hat{N}]}]. \quad (3.11)$$

The work done on the electrons when the field is changed adiabatically from value s_1 to value s_2 is $\Delta\tilde{G}(\beta, \mu) = \tilde{G}(\beta, \mu, s_2) - \tilde{G}(\beta, \mu, s_1)$. Therefore, from Eqs. (2.14) and (3.11),

$$\langle\hat{O}\rangle_{\text{exact}} = \left.\frac{\partial\tilde{G}}{\partial s}\right|_{s=0}. \quad (3.12)$$

Thus emerges an interpretation of the ensemble average value of \hat{O} , it is the *rate of work* done on electrons when turning on the field s . Once we have expressed any average value in terms of work, we can use the optimized effective free energy, which we postulate to also have the meaning of work, to produce an effective free-energy approximation for average values.

We now show that it is consistent with this work interpretation to simply take all averages in the noninteracting particle system. When the energy due to the field s is introduced, the definition of the Γ energy becomes

$$\tilde{\Gamma}(\beta, \mu, s) = \tilde{G}_0(\beta, \mu, s) + \langle\hat{H} + s\hat{O} - \tilde{H}_0\rangle, \quad (3.13)$$

where $\tilde{H}_0 = \tilde{h}^T\rho$ and \tilde{h} is the optimized Fockian matrix in the presence of the perturbation. Of course, this optimized Fockian now depends on s , however, because $\tilde{\Gamma}$ is insensitive to changes of \tilde{h} at optimum [see Eq. (3.8)], we find

$$\left. \left(\frac{\partial \tilde{\Gamma}}{\partial s} \right) \right|_{s=0} = \left. \left(\frac{\partial \tilde{\Gamma}}{\partial s} \right) \right|_{\tilde{h}, s=0}. \quad (3.14)$$

On the right, the derivative with respect to s is taken while \tilde{h} is held constant at its $s=0$ value. Once \tilde{h} is held constant, only terms *explicitly* depending on s in (3.13) contribute to the derivative. Since $s\hat{O}$ is the only one such term, we find

$$\left. \left(\frac{\partial \tilde{\Gamma}}{\partial s} \right) \right|_{s=0} = \langle \hat{O} \rangle, \quad (3.15)$$

which is consistent with the exact expression in Eq. (3.12).

The conclusion from Eq. (3.15) is that all ensemble average values in our approximation are to be *taken in the noninteracting system*,

$$\langle \hat{O} \rangle = \frac{1}{Z_0} \text{tr}[e^{-\beta(\hat{H}_0 - \mu\hat{N})} \hat{O}]. \quad (3.16)$$

We now return to the question posed in Eq. (3.10); which of the two expressions are we going to take? Our discussion above shows that it is the left one. What about the right one? Can we not use the analog of Eq. (2.15) in the optimized effective free energy? Let us take the derivative of Γ with respect to μ . We obtain from Eq. (2.26), after some manipulations,

$$\langle N \rangle + \left(\frac{\partial \Gamma}{\partial \mu} \right)_{\beta} = \beta [\langle (\hat{H} - \hat{H}_0) \hat{N} \rangle - \langle H - H_0 \rangle \langle N \rangle]. \quad (3.17)$$

Using Eq. (3.6), we see that the left-hand side vanishes and indeed both expressions in Eq. (3.10) are equal and thus correct.

C. The effective force on nuclei

The fact that Γ is a *variational* approximation to G allows us to use it as an approximate work function. When a nucleus is pushed adiabatically from \mathbf{R} to $\mathbf{R} + \delta\mathbf{R}$ the effective (average) work done on the electrons is approximated by

$$\delta W = \left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle \cdot \delta \mathbf{R}. \quad (3.18)$$

In the accurate calculation, the average force is conservative, i.e., the gradient of the exact free energy [Eq. (2.20)]. Because Γ is a variational approximation to G , the effective electronic force on the nuclei $\langle \delta \hat{H} / \delta \mathbf{R} \rangle$ in Eq. (3.18) is conservative as well. To see this, let us first note that the average force can be written as

$$\begin{aligned} \left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle &= Z_0^{-1} \text{tr} \left[e^{-\beta(\hat{H}_0 - \mu)} \frac{\delta \hat{H}}{\delta \mathbf{R}} \right] \\ &= \frac{\delta}{\delta \mathbf{R}} (Z_0^{-1} \text{tr}[e^{-\beta(\hat{H}_0 - \mu)} \hat{H}])_h, \end{aligned} \quad (3.19)$$

where the last derivative is taken with h (or equivalently \hat{H}_0) held constant. We thus find

$$\left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle = \left(\frac{\delta E}{\delta \mathbf{R}} \right)_h. \quad (3.20)$$

Taking the derivative of $E = \langle \hat{H} \rangle$ at constant h is easily shown [using Eq. (3.8)] to be equal to the derivative of the effective free energy, arriving at the result

$$\left\langle \frac{\delta \hat{H}}{\delta \mathbf{R}} \right\rangle = \frac{\delta \Gamma}{\delta \mathbf{R}}. \quad (3.21)$$

We thus find that the effective force is conservative and the work associated with it is the optimized effective free energy Γ .

IV. EXAMPLES

After presenting the details of the theory and numerical algorithms, we now turn to a demonstration of the formalism on actual molecular systems. We used standard Gaussian basis sets and computed the T and V matrices [Eqs. (2.4) and (2.7)] using the program GAMESS.³³ Note that from these we need to compute the matrix t using Eq. (2.7). The numerical solution of Eq. (3.5) is obtained by invoking a minimizing algorithm for Γ , using the gradient of Eq. (3.2), based on the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS) method implemented in Ref. 34.

Since the scaling of the present approach is the same as that of a Hartree–Fock calculation, the two methods have comparable computation times. The Hartree–Fock Fockian is a good initial guess for the Γ minimizing algorithm at high β (low temperature). Often it is necessary to perform several minimizations, starting from high value of β , gradually lowering β to the desired final value. At each minimization we take the field obtained from the previous iteration as an initial guess. Thus, the total cost of an effective free-energy calculation is a few times that of a Hartree–Fock computation.

We first treat in subsection IV A a system which can be treated *exactly*, i.e., H_2 in a small (double-zeta) basis. We then describe in subsection IV B using the new method the effect of temperature on the H_2O bending motion.

A. The hydrogen system

In order to assess the quality of the approximation, we used it in a simple setting, where exact results are available. We examined the H_2 molecule (internuclear distance of 0.7 Å) within a standard double-zeta (DZV) basis having $M=4$ orbitals. The maximal number of electrons is thus $2M=8$ leading to a total of $2^{2M}=256$ electronic states. The exact (within the basis set) free energy $G(\beta, \mu)$ is computed by full configuration interaction, i.e., calculations of all fully correlated 256 states using the GAMESS code.³³ This free energy is plotted in Fig. 1 as a function of the chemical potential μ for several values of β . The function is monotonic nonincreasing and convex upwards, since $-\partial G / \partial \mu$ is the electron number, a non-negative quantity [Eq. (2.15)] and since $\partial^2 G / \partial \mu^2$ is negative [Eq. (2.17)].

The exact average electron number $N_{\text{exact}}(\beta, \mu)$ obtained from the full configuration-interaction (FCI) calculation is

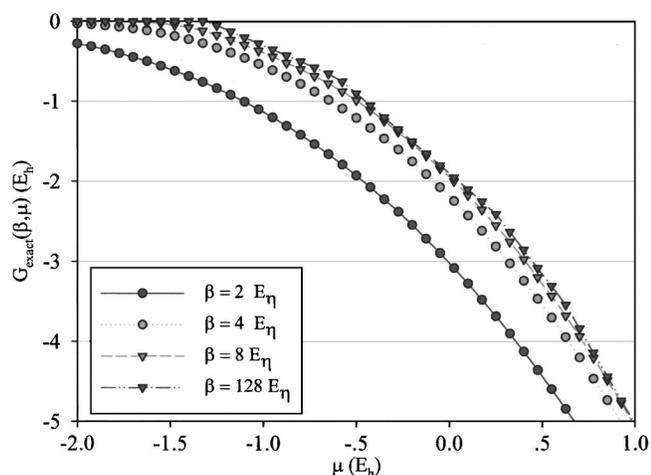


FIG. 1. The exact free energy for the H_2 molecule (in DZV basis) as a function of the chemical potential for several values of β .

shown in Fig. 2. At low temperatures the staircase shape is evident where only quantized integer values of N are allowed. The width of the stair $\Delta\mu$ multiplied by the corresponding quantized N is the free energy necessary to add an electron (going from N to $N+1$ electrons). At higher temperatures this interpretation is only approximate and gradually the stair structure is destroyed.

The quality of the approximation can be assessed by considering the correlation free energy, $\Delta G(\beta, \mu) = G(\beta, \mu) - \Gamma(\beta, \mu)$. To facilitate the comparison, we plot $\Delta G(\beta, \mu)$ as a function of $N(\mu)$ in Fig. 3. At the $N \rightarrow 0$ and $N \rightarrow 2M$ limits, $\Delta G \rightarrow 0$ and the result is exact, a general rule. As $\beta \rightarrow \infty$ the $N=1$ and $N=2M-1$ become exact as well, since for a single electron/hole there is no electron correlation in the ground state. Furthermore, in the low-temperature limit $\beta \rightarrow \infty$, ΔG approaches the ground-state correlation energy, i.e., the difference between the Hartree–Fock energy and the exact ground-state energy, which, for $N=2$ is around $-0.03E_h$ for this basis set. In general, when the temperature increases there is a larger difference (even when the average electron number is $N=1$). We see in Fig. 3 that at not too high tem-

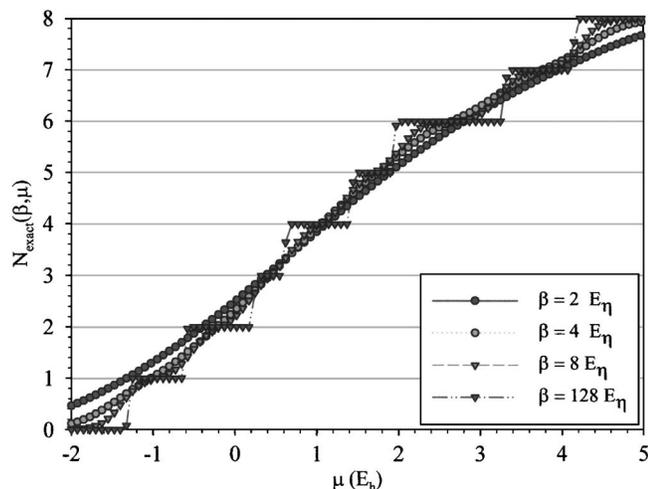


FIG. 2. The number of electrons as a function of chemical potential for several temperatures for the H_2 molecule in a DZV basis.

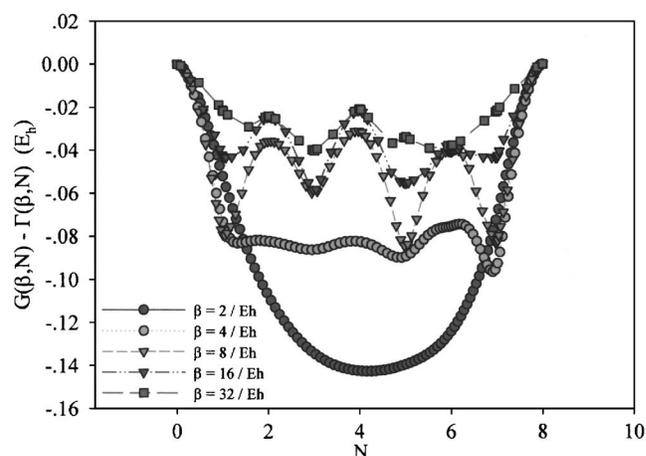


FIG. 3. The difference between the exact and optimized effective free energy for the H_2 molecule in a DZV basis set.

peratures, the maximal differences appear at odd integer values of N and minimal differences at even values of N . This shows that structures with dominant open-shell character are not described as well by the approximation. This is in spite of our use of a spin-unrestricted formalism, that is, the α and β components of u are not constrained to be identical.

The difference between the exact average number of electrons and that derived from the approximation is shown Fig. 4. At not too high temperatures the minimal differences in electron count appear at integer electron count while maximal deviations appear at transition regions between the staircase steps in Fig. 2, i.e., at half integer electron number values. Here, the average charge of the system changes abruptly and thus there is high sensitivity to any approximation. At high temperatures the errors in average charge are smaller and smoother.

We now examine the potential-energy curve of H_2 . We compare several values of the temperature at a given chemical potential in Fig. 5 (top). At sufficiently high temperatures the bond length is affected as the temperature grows. At the highest temperature shown $\beta = 6E_h^{-1}$, $T = 52.6 \times 10^3$ K the bond length has grown to 0.84 \AA . As the temperature is

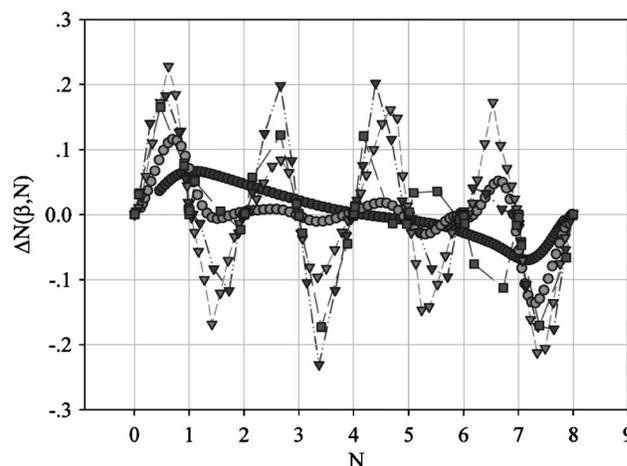


FIG. 4. The difference between the exact and approximate number of electrons as a function of the number of electrons for several values of the temperature (same legend as Fig. 3).

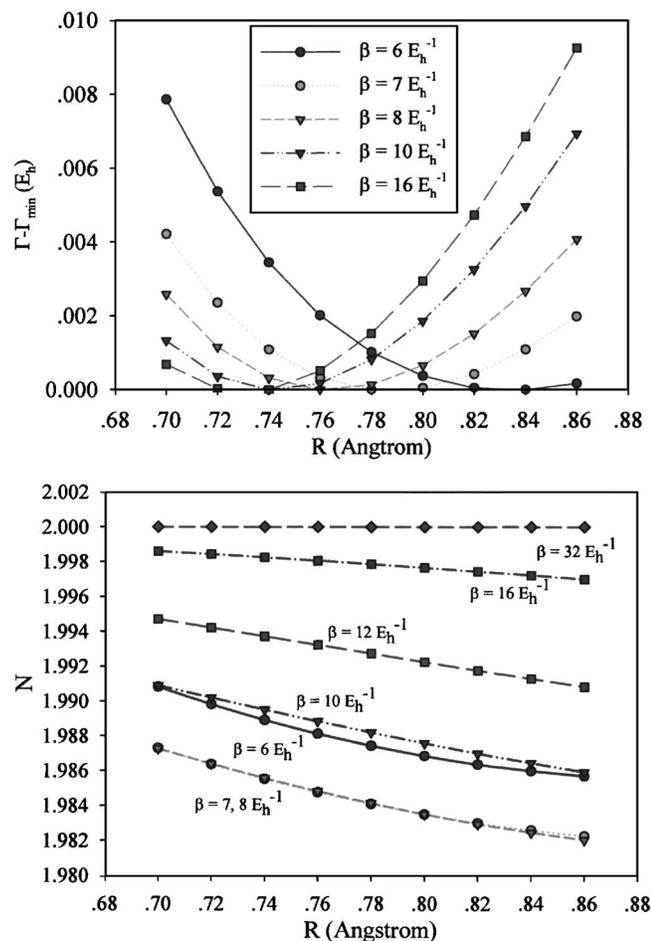


FIG. 5. The effective free-energy potential curve (top) and average electron number (bottom) for H_2 at $\mu = -0.2E_h$ shown for various temperature parameters.

raised, the potential curve slightly flattens. This is due to the population of the lower excited states which have “antibonding” or repulsive character. The electron count decreases with increasing bond length. Interestingly, for a given bond length, the electron count as a function of temperature is nonmonotonic. At $\beta \geq 32E_h^{-1}$ the electron count is practically 2. When $\beta = 16E_h^{-1}$, N is slightly less than 2 and continues to decrease, until $\beta \approx 7.5E_h$, where a further decrease in β causes a fast growth in N . At $\beta = 4E_h^{-1}$, $N \approx 2.01$ and at $\beta = 2E_h^{-1}$, $N \approx 2.2$. Initially, when the temperature grows, the higher lying ionized H_2^+ states become accessible and the molecule tends to loose electronic population. At still higher temperatures a dense manifold of negatively charge states is being populated and thus the number of electrons grows.

To summarize, we have shown that the OEFE is a reasonable approximation to the exact free energy. Several observables were studied and compared, showing a good agreement. In particular, we showed that high temperatures strongly affect the shape of the free-energy potential curve as a function of nuclear separation.

B. The water system

We now examine a slightly more complex system, namely, the water molecule. For this molecule a DVZ basis

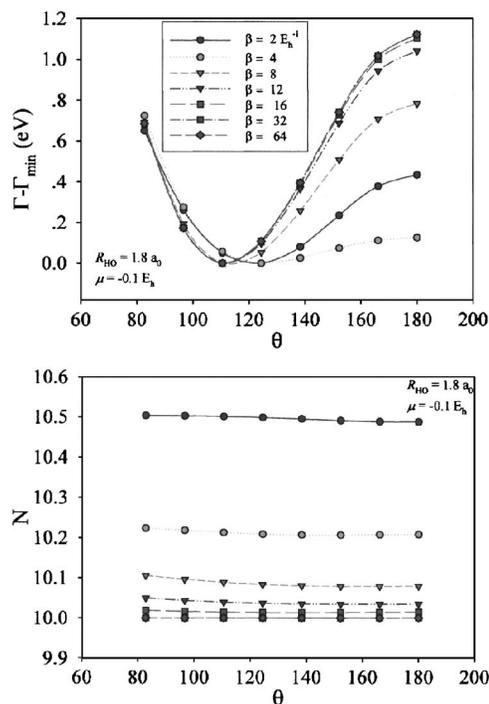


FIG. 6. The bending potential curves (top) and average electron number (bottom) for H_2O for several values of β . Chemical potential is $\mu = -0.1E_h$ and OH distance is $1.8a_0$. Potential curves are shifted to a common minimal energy to facilitate comparison.

was used, taking a fixed OH bond length of $1.8a_0$ and varying the HOH angle θ . We chose a chemical potential of $\mu = -0.1E_h$, since it assures an average of ten electrons at low temperatures (we discuss the electron number below). We computed the effective optimized free energy as a function of the bonding angle θ and the temperature β . The results are shown in Fig. 6. The potential curve is essentially identical with the unrestricted Hartree–Fock ground-state potential at $\beta \geq 32E_h^{-1}$. As β is reduced (temperature grows) the potential changes, at first flattening and then developing a new minimum at a HOH angle of $\theta \approx 125^\circ$. It is interesting to note that the $\beta = 4E_h^{-1}$ curve is more flat than the $\beta = 2E_h^{-1}$ curve, although both show a minimum at the same place.

The dependence of the number of electrons on the temperature is examined in the bottom panel of Fig. 6. It is seen that the average number of electrons grows with increasing temperature. This behavior is different from the H_2 result where the number of electrons initially drops. The exact behavior of N as a function of β is sensitively dependent on the structure of the neutral and ionic (anionic and cationic) energy manifolds. Interpretation in simple terms of these results is thus not an easy task.

The potential curves in Fig. 6 are made for constant μ . It is interesting to compare with the potential for a process where N rather than μ is kept constant. The former is the approximate Helmholtz energy $\alpha(\beta, N) = \Gamma + N\mu$, discussed in some detail in Appendix A. In Fig. 7 we compare the Γ and α potentials for $\beta = 8E_h^{-1}$. The value of α is computed by searching for the value of μ for which $N(\mu) = 10$, using an interpolation between three values of $N(\mu)$, for $\mu = 0, -0.1$, and $-0.2E_h$. In general the α and Γ potentials can differ

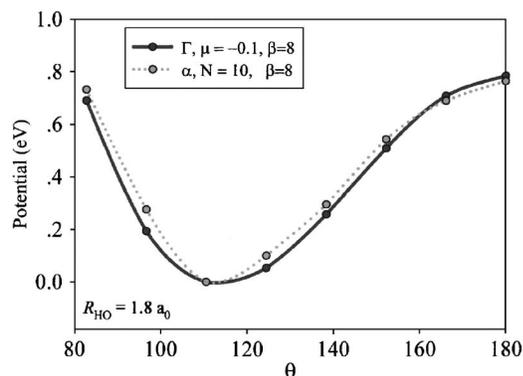


FIG. 7. Comparison of the potential curve approximations based on the Gibbs free energy Γ and the Helmholtz free energy α . (The curves are shifted to a common minimal energy.)

substantially, however, in this specific case it is seen that both are very similar, most likely because of the small change in number of electrons at $\beta = 8E_h^{-1}$.

V. PROSPECTIVES

In this article we focused on a general account of the principles of the method. We have only given a small set of demonstrations. In future publications we intend to use the theory for applications where the open system nature of the method is important. Several such prospect cases are briefly discussed here.

A. Molecular dynamics at high temperatures

Molecular dynamics at high temperatures may be of interest in many applications, such as studies of shockwave during explosion, dynamics of hot plasmas and flames,^{1,2,6,7} and dynamics ensuing exposure to strong laser fields.³⁵ By high temperatures we mean those for which $k_B T$ is comparable to the energy differences between the ground and low-lying excited electronic states. If the electronic manifold is sufficiently dense at these temperatures, the electronic relaxation processes should be fast and it may be reasonable to assume that nuclei are acted upon by an average force of the electrons. In such regimes the free energy $G(\mathbf{R}_1, \mathbf{R}_2, \dots)$ acts as an effective potential surface. We have seen that this potential surface is highly sensitive to the temperature.

B. Improving QM/MM and embedding in metals

The present method will be helpful for various embedding methods. For example, when a molecule is adsorbed on a metal surface, it is often modeled by a small cluster of metal atoms.^{10,36} By enlarging the cluster it is hoped that the adsorbed molecule properties will converge. However, usually this is not the case and extremely large clusters need to be used. Since the electronic screening is very effective in metals, the convergence problems are not a result of long-range interactions. Instead, at least part of the problem has more to do with the nonlocal nature of electrons in the metal. The slow convergence of the adsorbate properties may be due to the fact that any finite cluster, since it is part of a larger system, has a noninteger number of electrons (on the

average). Most methods, however, enforce integer number of electrons for any finite cluster and therefore a huge cluster is required. One embedding method not suffering from this disadvantage is the dipped adcluster model.¹² The method presented in this paper can be applied in a similar manner, and being a rigorous theory, it is likely to yield even better results.

Quantum-mechanical/molecular mechanical (QM/MM) methods³⁷⁻⁴¹ also use various types of embedding schemes. They have become a most popular approach for theoretical studies of biochemical systems. In the QM/MM approach, a large biochemical molecule (such as a protein) is divided into two parts. A small active site which is of interest because of its important (reactive) biological role and a much larger part which has non-negligible effects on the electronic structure of the active site via direct (structural) interaction as well as long-range electrostatic interactions. In QM/MM the bonds of the active site are disconnected from the rest of the molecule. The resulting dangling bonds are then saturated by, e.g., hydrogen atoms. The chemically isolated reactive site is still exposed to the existing external electrostatic fields of the environment (usually modeled as point charges). The active site electronic structure is then determined quantum mechanically by an *ab initio* or semiempirical electronic structure method.

What present QM/MM approaches miss is once again, the fact that the isolated QM part should have the chemical potential of the environment. This means that it may be (on the average) partially charged. Because the effect of chemical potential is not taken into account in most QM/MM calculations researchers may have to increase the size of the QM part, making their calculation expensive.

C. Self-Interaction correction in density-functional theory

There are a few density-functional applications within an electronic Helmholtz free-energy^{15,42,43} formalism. These are based on the ensemble density-functional theory⁴⁴ (DFT) and the underlying exchange-correlation (XC) functional is local (such as the local-density approximation⁴⁵ or the generalized gradient approximation⁴⁶). The developments are considerably simpler than here due to the locality of the functional. The present method can be adapted quite straightforwardly to deal with DFT. However, it is more powerful than that. It is well known that excited states and anions cannot be reasonably approximated within local DFT because of the self-interaction problem.⁴⁷⁻⁴⁹ Correcting for this problem will typically necessitate introduction of explicit (so-called “exact”) exchange into the XC functionals.^{49,50} The present method has no problem in accommodating such a self interaction correction. In DFT, such nonlocal functionals are often treated within the optimized potential method of Talman and Shadwick.⁵¹ The formalism in this paper can be changed to accommodate the search for an optimized effective potential in these cases. This is done by constraining the search for a minimum of $\Gamma[u]$ only to matrices u that represent potentials, i.e., commutative with the electron position operators \hat{x} , \hat{y} , and \hat{z} . Such constraints can be enforced using, e.g., the

augmented Lagrange multiplier technique.⁵² Thus, the present approach can be viewed as a precursor for a general framework treating various functionals with local, nonlocal, and explicit exchange functionals at various temperatures. The ground-state results can be obtained by taking the zero-temperature limit.

D. Molecular electronics: Molecular bridges under bias

The conductance of electricity through a single molecule chemically connected to two metallic leads has been the subject of intense research in recent years.^{13,14,19,53–57} The common theoretical description assumes that the macroscopic leads are each characterized by a chemical potential μ_L for the “left” lead and μ_R for the right lead. The electricity flows as a result of the difference in the chemical potentials. The difficult part of the calculation is to account for the charge distributions on the bridge molecule under this chemical-potential bias. The present formalism makes a step towards a self-consistent approach in this problem. While here we are describing only a system with one chemical potential, the formalism has the capacity to be extended to describe the system with two chemical potentials. This will be done by selecting two sets of localized basis function for each subsystem.

E. Shift for the open system auxiliary field Monte Carlo

Since the present method already gives good free-energy estimates, the additional “correlation-energy” corrections can be made using various many-body theories. One way is to use the shifted contour auxiliary field Monte Carlo (SCAFMC) method.^{28,58–60} In this method, a Hubbard–Stratonovich^{61,62} transformation is invoked, leading to a multidimensional integral for the free energy, which is then estimated using Monte Carlo methods. A critical additional component is the shifted contour,⁵⁹ which reduces the strong statistical fluctuations. In zero-temperature calculations the shifting field is taken from the Hartree–Fock approximation. Such an approach has led to successful applications of SCAFMC in a variety of cases.^{58–60,63–66} The method presented in this paper can give a good contour shift for application with SCAFMC in open system conditions. Application of this idea is currently being studied in our group.

VI. SUMMARY

We have presented a variational method for treating the electronic structure of molecules under conditions of an open system characterized by a chemical potential and a temperature. The method builds an effective optimized free energy for the electrons, which allows approximate determination of the average electronic properties and effective forces on the nuclei. We have demonstrated the theory on two small molecular systems. It should be noted that both these systems have rather large energy spacings (excitation energies of the order of 10 eV). Thus temperature effects are observed mainly in the $T \approx 30\,000$ -K regime ($\beta \approx 10E_h^{-1}$). Still, many

systems have a lower excitation energy manifold and thus strong temperature effects can be observed even at much lower temperatures. In metals, for example, temperature effects will be strong even below room temperature.

The numerical effort in the method we presented scales as $O(M^4)$, similar to the complexity of the Hartree–Fock method within Gaussian basis-set methods. It is probable that the relatively high scaling can be reduced dramatically using linear scaling techniques developed for Hartree–Fock and density-functional theory,^{52,67–69} which are based on the sparsity of the density matrix $\langle \hat{\rho}_1 \rangle$, a feature enhanced at high temperatures.

ACKNOWLEDGMENTS

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APPENDIX A: HELMHOLTZ FREE ENERGY

The grand-canonical ensemble only allows for a chemical potential to be specified. The number of electrons is determined by the free energy. Such a situation is natural for open systems, but there are physical problems where the system is closed and can only exchange heat (but not particles) with an external reservoir. In such cases, the canonical ensemble is more useful and the appropriate free energy is the Helmholtz free energy defined by

$$A(\beta, N) = -\beta \ln Q(\beta, N), \quad (\text{A1})$$

with

$$Q(\beta, N) = \text{tr}_N e^{-\beta H}. \quad (\text{A2})$$

One can use the Gibbs–Peierls–Bogoliubov inequality to derive a variational approximation for A , along with very similar lines as before. However, this approach would not be easy to apply since the theory involves taking canonical traces involving $\binom{M}{N}$ states for a system of N electrons. This high scaling is not present in the grand-canonical ensemble, as discussed in Sec. II B. As for the Gibbs energy, A has the property that it is the work potential function for processes done at constants β and N .

Since the canonical approach is complicated, an alternative approach would be to obtain an energy function which has the property that it describes the work for processes under constant N and is *compatible* with the work derived from the OEFE. Consider the function,

$$\alpha(\beta, N) = \Gamma(\beta, \mu) + \mu N. \quad (\text{A3})$$

For an infinite system this function is equal to the Helmholtz free energy. But that is not so for finite systems. Nevertheless, it is useful. In Eq. (A3) μ is now a function of β and N , determined by the condition,

$$\left. \frac{\partial \Gamma}{\partial \mu} \right|_{\beta, \mu(\beta, N)} = -N. \quad (\text{A4})$$

When \mathbf{R} is changed by $\delta \mathbf{R}$ under constant N , we have

$$\frac{\delta\alpha}{\delta\mathbf{R}} = \frac{\delta\Gamma}{\delta\mathbf{R}} + N \frac{\delta\mu}{\delta\mathbf{R}}. \quad (\text{A5})$$

Expanding the first term on the right, we find

$$\frac{\delta\Gamma}{\delta\mathbf{R}} = \frac{\partial\Gamma}{\partial\mathbf{R}} + \frac{\partial\Gamma}{\partial\mu} \frac{\delta\mu}{\delta\mathbf{R}}, \quad (\text{A6})$$

using (A4), we find

$$\frac{\delta\alpha}{\delta\mathbf{R}} = \frac{\partial\Gamma}{\partial\mathbf{R}}. \quad (\text{A7})$$

Since $\delta\Gamma/\delta\mathbf{R}$ is the effective force on the nuclei when the system has N electrons, we find that $\delta\alpha/\delta\mathbf{R}$ is also of *that same force*. We conclude that α is a potential function for the motion of the nuclei at constant average number of electrons. This function as defined in (A3) is such a potential which is compatible with the OEFE Γ . Computing α is not as straightforward as computing Γ . It can be done by interpolation methods to locate the μ that gives the required integer number of particles.

APPENDIX B: GRADIENT OF THE EFFECTIVE FREE ENERGY

In this appendix we discuss the formal development allowing the computation of the derivative of the effective free energy $\Gamma[U]$, given in Eq. (3.1) with respect to U_I (where I is an index of an element of U). The resulting quantities will be ensemble averages, whose evaluation is described in Appendices C and D. In taking the gradient of Eq. (3.1), we find

$$\frac{\delta\Gamma}{\delta u_I} = \frac{\delta G_0}{\delta u_I} + \frac{1}{2} V_{JK} \frac{\delta}{\delta u_I} \langle \hat{\rho}_J \hat{\rho}_K \rangle - \langle \hat{\rho}_I \rangle - u_I \frac{\delta \langle \hat{\rho}_I \rangle}{\delta u_I}. \quad (\text{B1})$$

All these derivatives can be evaluated based on the formal derivative for the exponential operator $e^{-\beta\hat{H}_0}$, where \hat{H}_0 is the operator given in Eq. (2.21). Standard time-dependent perturbation theory shows that

$$\frac{\delta}{\delta u_I} e^{-\beta\hat{H}_0} = - \int_0^\beta e^{-\hat{H}_0(\beta-\beta')} \hat{\rho}_I e^{-\hat{H}_0\beta'} d\beta' \equiv -\beta e^{-\hat{H}_0\beta} \bar{\rho}_I, \quad (\text{B2})$$

where

$$\bar{\rho}_I = \frac{1}{\beta} \int_0^\beta e^{\hat{H}_0\beta'} \hat{\rho}_I e^{-\hat{H}_0\beta'} d\beta'. \quad (\text{B3})$$

From this, we find after a short calculation that

$$\frac{\delta G_0}{\delta U_I} = - \langle \bar{\rho}_I \rangle = - \langle \hat{\rho}_I \rangle. \quad (\text{B4})$$

Using Eq. (B2), it is straightforward to prove also that

$$\frac{\delta}{\delta u_I} \langle \hat{\rho}_I \rangle = \beta [\langle \hat{\rho}_I \rangle \langle \hat{\rho}_I \rangle - \langle \bar{\rho}_I \hat{\rho}_I \rangle], \quad (\text{B5})$$

as well as

$$\frac{\delta}{\delta u_I} \langle \hat{\rho}_J \hat{\rho}_K \rangle = \beta [\langle \hat{\rho}_I \rangle \langle \hat{\rho}_J \hat{\rho}_K \rangle - \langle \bar{\rho}_I \hat{\rho}_J \hat{\rho}_K \rangle]. \quad (\text{B6})$$

Plugging these identities into Eq. (3.1) yields Eq. (3.2).

APPENDIX C: ENSEMBLE AVERAGES

Here we speak of *one-body Hamiltonians* $\hat{H}_0 = h_I \hat{\rho}_I$ and show how to compute grand-canonical averages of products of operators with this Hamiltonian. We have

$$Z = \sum_N e^{\beta\mu N} \text{tr}_N [e^{-\beta\hat{H}_0}] = \det(1 + W), \quad (\text{C1})$$

where

$$W = e^{\beta(\mu-h)}. \quad (\text{C2})$$

Now, let \hat{A} be another one-body operator. Its grand-canonical (GC) average

$$\langle \hat{A} \rangle = Z^{-1} \text{tr} [e^{-\beta(\hat{H}_0 - \mu\hat{N})} \hat{A}] \quad (\text{C3})$$

will be calculated using the identity

$$\hat{A} = \left. \frac{d e^{\hat{A}t}}{dt} \right|_{t=0}. \quad (\text{C4})$$

Thus

$$\langle \hat{A} \rangle = Z^{-1} \left. \frac{d}{dt} \text{tr} [e^{-\beta(\hat{H}_0 - \mu\hat{N})} e^{\hat{A}t}] \right|_{t=0}. \quad (\text{C5})$$

Now, since $e^{-\beta\hat{H}} e^{t\hat{A}}$ is itself *the exponent* of a one-body operator,

$$\langle \hat{A} \rangle = Z^{-1} \left. \frac{d}{dt} \det[1 + W e^{tA}] \right|_{t=0}. \quad (\text{C6})$$

Using the well-known relation,

$$\det X = e^{\text{Tr}[\ln X]}, \quad (\text{C7})$$

we obtain after a short calculation,

$$\langle \hat{A} \rangle = \left. \frac{d}{dt} \text{Tr}[\ln(1 + W e^{tA})] \right|_{t=0}. \quad (\text{C8})$$

(Note that we use the symbol tr to denote a trace over many-body states, while the symbol Tr is reserved to denote the matrix trace of $M \times M$ matrices.) Expanding the exponent to linear order in At , we have

$$e^{At} = 1 + At + O(t^2). \quad (\text{C9})$$

Using this, after a short manipulation, it is possible to show

$$\langle \hat{A} \rangle = \left. \frac{d}{dt} \text{Tr}[\ln((1 + W)(1 + DAt + O(t^2)))] \right|_{t=0}, \quad (\text{C10})$$

where

$$D = (1 + W)^{-1} W. \quad (\text{C11})$$

Note also that

$$1 - D = (1 + W)^{-1}. \quad (\text{C12})$$

To continue, we use the identity,

$$\text{Tr}[\ln[e^X e^Y]] = \text{Tr}[X + Y] \quad (\text{C13})$$

[this relies on the fact that $\det(e^X e^Y) = \det(e^X)\det(e^Y)$] and

$$\ln(1 + Xt) = Xt + O(t^2). \quad (\text{C14})$$

in Eq. (C10) giving

$$\begin{aligned} & \text{Tr}[\ln((1 + W)(1 + DA + O(t^2)))] \\ &= \text{Tr}[\ln(1 + W) + DA] + O(t^2). \end{aligned} \quad (\text{C15})$$

Finally, taking the derivative of (C15), afterwards setting $t = 0$ we find

$$\langle \hat{A} \rangle = \text{Tr}[DA]. \quad (\text{C16})$$

Next we consider $\langle \hat{A}\hat{B} \rangle$, where \hat{B} is also a one-body operator. We will not present all stages of the calculation starting from,

$$\langle \hat{A}\hat{B} \rangle = Z^{-1} \frac{d^2}{dt ds} \det(1 + We^{tA} e^{sB})|_{t,s=0}. \quad (\text{C17})$$

Working out the algebra, using the same ideas we presented above, it is possible to arrive at

$$\langle \hat{A}\hat{B} \rangle = \langle \hat{A} \rangle \langle \hat{B} \rangle + \text{Tr}[DA(1 - D)B]. \quad (\text{C18})$$

In the gradient expression (3.2) we need not the average $\langle \hat{A}\hat{B} \rangle$ but the cumulate average,

$$\langle \hat{A} \rangle \langle \hat{B} \rangle - \langle \hat{A}\hat{B} \rangle = -\text{Tr}[DA(1 - D)B]. \quad (\text{C19})$$

It is interesting to note that the matrix representing \hat{A} appears here in the following form:

$$\check{A} = DA(1 - D), \quad (\text{C20})$$

(we term \check{A} as ‘‘A smiley’’). This is an important observation which bares on a stable numerical evaluation of these expressions, as discussed below. Thus, we write

$$\langle \hat{A} \rangle \langle \hat{B} \rangle - \langle \hat{A}\hat{B} \rangle = -\text{Tr}[\check{A}B]. \quad (\text{C21})$$

The expectation value of a product of three operators can be developed along similar lines to yield

$$\begin{aligned} \langle \hat{A}\hat{B}\hat{C} \rangle &= \text{Tr}[DA]\text{Tr}[DB]\text{Tr}[DC] + \text{Tr}[DA]\text{Tr}[DB(1 - D)C] \\ &+ \text{Tr}[DC]\text{Tr}[DA(1 - D)B] \\ &+ \text{Tr}[DB]\text{Tr}[DA(1 - D)C] \\ &+ \text{Tr}[(A(1 - D)B - BDA)(1 - D)CD]. \end{aligned} \quad (\text{C22})$$

In the gradient expression (3.2), we actually need only the expression $\langle \hat{A}\hat{B}\hat{C} \rangle - \langle \hat{A} \rangle \langle \hat{B}\hat{C} \rangle$, finding a more compact expression

$$\begin{aligned} \langle \hat{A}\hat{B}\hat{C} \rangle - \langle \hat{A} \rangle \langle \hat{B}\hat{C} \rangle &= \text{Tr}[DC]\text{Tr}[\check{A}B] + \text{Tr}[DB]\text{Tr}[\check{A}C] \\ &+ \text{Tr}[\check{A}(B(1 - D)C - CDB)]. \end{aligned} \quad (\text{C23})$$

Once again, the matrix representing \hat{A} appears in this expression only in terms of the smiley-A matrix \check{A} (again, this is important for the stable numerical evaluation of the expressions).

APPENDIX D: WORKING EXPRESSIONS

In this appendix we discuss the actual calculation of expectation values of one-, two-, and three-body operators that appear in the expressions derived in the previous appendix. We showed that in all expressions for expectation values of such operators [(C8) and (C22)], we do not really need the matrix elements of the operator $\bar{\rho}$. Instead, we expressed the required averages in terms of the smiley matrix elements of $\check{\rho} = D\bar{\rho}(1 - D)$, where D is the Fermi–Dirac density matrix,

$$D = (1 + W)^{-1} W = \frac{e^{\beta(\mu - \varepsilon)}}{1 + e^{\beta(\mu - \varepsilon)}}. \quad (\text{D1})$$

Since $\bar{\rho}$ by itself might have huge and tiny matrix elements causing numerical instabilities, we concentrate on the better behaved matrix $\check{\rho}$, which is computed as follows. We define K as the orthogonal matrix of eigenvectors of h and ε a diagonal matrix of its eigenvalues. Thus $h = T + U = K\varepsilon K^T$. Using these, we define

$$r_I \equiv K^T \check{\rho}_I K = K^T D K K^T \bar{\rho}_I K K^T (1 - D) K. \quad (\text{D2})$$

Plugging in (D1), and using the definition of $\bar{\rho}$ [Eq. (B2)] we find

$$r_I = \frac{e^{\beta(\mu - \varepsilon)}}{(1 + e^{\beta(\mu - \varepsilon)})} \frac{1}{\beta} \int_0^\beta e^{\beta' \varepsilon} K^T \rho_I K e^{-\beta' \varepsilon} d\beta' \frac{1}{(1 + e^{\beta(\mu - \varepsilon)})}. \quad (\text{D3})$$

Here ρ_I is the matrix elements of $\hat{\rho}_I$. Because all matrices involving ε are diagonal, we can perform the integration analytically, obtaining the relation,

$$[r_I]_{lm} = R_{lm} [K_{il} K_{i'm}], \quad (\text{D4})$$

where $I = (i, i')$ and

$$R_{lm} = \frac{e^{\beta(\mu - \varepsilon_l)}}{1 + e^{\beta(\mu - \varepsilon_l)}} \begin{cases} \frac{e^{\beta(\varepsilon_l - \varepsilon_m)} - 1}{(1 + e^{\beta(\mu - \varepsilon_m)})\beta(\varepsilon_l - \varepsilon_m)} & \varepsilon_l \neq \varepsilon_m \\ \frac{1}{1 + e^{\beta(\mu - \varepsilon_l)}} & \varepsilon_l = \varepsilon_m \end{cases}. \quad (\text{D5})$$

It is straightforward to verify that R is a symmetric matrix. In actual calculations, to avoid numerical problems, we compute only R_{lm} when $\varepsilon_l < \varepsilon_m$ and then set $R_{ml} \leftarrow R_{lm}$. This way of evaluating (D5) leads to stable numerical results, because $e^{\beta(\mu - \varepsilon_l)} / [(1 + e^{\beta(\mu - \varepsilon_l)})(1 + e^{\beta(\mu - \varepsilon_m)})]$ is always a number between 0 and 1, and so is $e^{\beta(\varepsilon_l - \varepsilon_m)}$.

In deriving Eq. (D4) we also used the fact that

$$(\rho_I)_{kk'} = \delta_{ik} \delta_{i'k'}, \quad (\text{D6})$$

leading to

$$[K^T \rho_I K]_{lm} = K_{lk}^T [\rho_I]_{kk'} K_{k'm} = K_{il} K_{i'm}. \quad (\text{D7})$$

Building all matrices r_I is a $O(M^4)$ operation. Once each matrix r_I is built, then it is possible to write

$$\check{\rho}_I = K[r_I]K^T. \quad (\text{D8})$$

Since the overall computation of all $\check{\rho}_I$ matrices scales as $O(M^5)$, we do not actually build them. Instead, we use the fact that for any matrix X ,

$$\text{Tr}[\check{\rho}_I X] = \text{Tr}[r_I K^T X K], \quad (\text{D9})$$

and note that using the right-hand expression, the evaluation of each trace requires $O(M^2)$ operations, and since there are M^2 such traces, the overall effort is $O(M^4)$. For example, consider the numerically expensive term in the gradient Eq. (3.2), which using Eq. (C23) can be written as

$$\begin{aligned} & V_{JK}[\langle \hat{\rho}_I \rangle \langle \hat{\rho}_J \hat{\rho}_K \rangle - \langle \bar{\rho}_I \bar{\rho}_J \bar{\rho}_K \rangle] \\ &= V_{JK} \text{Tr}[\check{\rho}_I (2\rho_K D\rho_J - \rho_J \rho_K)] - V_{JK} [2 \text{Tr}[\check{\rho}_I \rho_J] \text{Tr}[D\rho_K]]. \end{aligned} \quad (\text{D10})$$

Computing, for example, $V_{JK} \text{Tr}[\check{\rho}_I \rho_K D\rho_J]$ scales as $O(M^4)$, as we show now. First, note that

$$V_{JK} \text{Tr}[\check{\rho}_I \rho_K D\rho_J] = V_{JK} [\check{\rho}_I]_{nl} (\rho_K)_{ll'} D_{l'l} (\rho_J)_{im}. \quad (\text{D11})$$

Then, since

$$(\rho_J)_{ll'} V_{JK} (\rho_K)_{i'l} = V_{ll' i' i}, \quad (\text{D12})$$

it is possible to write

$$V_{JK} [\langle \hat{\rho}_I \rangle \langle \hat{\rho}_J \hat{\rho}_K \rangle - \langle \bar{\rho}_I \bar{\rho}_J \bar{\rho}_K \rangle] = \text{Tr}[r_I \tilde{W}] \quad (\text{D13})$$

with $\tilde{W} = K^T W K$ and

$$W_{il} = V_{ijkl} [2D_{jk} - \delta_{jk}] - 2V_{iljk} D_{jk}. \quad (\text{D14})$$

Working along similar lines, the second term in the gradient of Eq. (3.2) is simply evaluated to

$$\text{Tr}[r_I K^T u K]. \quad (\text{D15})$$

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