Positivity Preserving Density Matrix Minimization for Fermi-Dirac States at Finite Temperatures

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We present methods for calculating the Fermi-Dirac density matrix for electronic structure problems at finite temperature while preserving physicality by construction. These methods model cooling a state initially at infinite temperature down to the desired finite temperature. We consider both the grand canonical ensemble (constant chemical potential) and highlight subtleties involved with treating the canonical ensemble (constant number of electrons) that have been overlooked in previous works. We hope that the discussion and results presented in this article reinvigorates interest in density matrix minimization methods.

I. INTRODUCTION

The ability to determine the electronic structure is of critical importance for obtaining a proper understanding of the quantum behavior of materials. One way of many to achieve this is by computing an effective single-electron density matrix $\hat{\rho}$ that statistically describes the system state in question. Once $\hat{\rho}$ has been determined, it can be used to obtain other information about the system such as the number of electrons $N_e = \text{Tr}(\hat{\rho})$ or the electronic energy $E = \text{Tr}(\hat{H}\hat{\rho})$, where $\hat{H}$ is the $N \times N$ Hamiltonian matrix, which in general depends upon $\hat{\rho}$.

Unfortunately, conventional methods for obtaining $\hat{\rho}$ are known to scale poorly with the size of the system. For such states $\hat{\rho}$ is localized, i.e., for orbitals $\phi_i$ and $\phi_j$, the element $\hat{\rho}_{ij} \to 0$ as the distance between them $R_{ij} \to \infty$. This means that the density matrix can be truncated so that elements where $R_{ij} > R_c$ are set to zero. The appropriate choice for $R_c$ will differ between insulators and metals. In general, metallic systems will require a larger value of $R_c$ to obtain accurate results because their orbitals have longer ranges than insulator systems.

The core idea of our methods is that the Fermi-Dirac state for the grand canonical ensemble at any temperature is the solution to the initial value problem for Eq. (1) and (10); whereas, the Fermi-Dirac distribution for the canonical ensemble solves the initial value problem given by Eqs. (25) and (21). Note that the solutions of Eqs. (1) and (20) by construction are positive matrices, hence we are guaranteed not to get spurious negative probabilities—a crucial physicality constraint. The developed methods are illustrated on a system described by a Hückel theory Hamiltonian (Sec. VA) and hydrogen fluoride (HF) (Sec. VB). The Hückel theory system serves as a useful benchmark for $\hat{\rho}$ represented in an orthogonal basis. In contrast, using HF allows us to test the ability of our methods to handle non-orthogonal bases and Hamiltonians that include the density functional theory corrections that depend upon $\hat{\rho}$. In Secs. V and VI we point out some “inconvenient truths” that may have plagued the development of DMM methods with a hope that it will lead to a new generation of DMM techniques.

II. FINITE TEMPERATURE DMM

We were motivated to consider an iterative approach for calculating $\hat{\rho}$ at finite temperatures by the method developed by Bloch [17] to obtain the Gibbs state $\hat{\rho}(\beta) = \exp\left(-\beta\hat{H}\right)$ and $\beta = 1/(kT)$ is the inverse temperature of the system. For such states

\[
\frac{d\hat{\rho}}{d\beta} = -\hat{H}\hat{\rho}.
\]

This equation along with the initial condition $\hat{\rho}(0) = 1$ (i.e. the identity matrix) can be used to construct an iterative method for finding $\hat{\rho}$ at any given temperature. The problem with using Eq. (1) is that numerical errors in the calculation may make $\hat{\rho}$ non-Hermitian. To avoid
this issue, Bloch symmeterized Eq. (1) in the following manner
\[ \frac{d \hat{\rho}}{d \beta} = -\frac{\hat{H}\hat{\rho}}{2} - \frac{\hat{\rho}\hat{H}}{2}. \] (2)

To elucidate the power of the Bloch method, let us prove that evolving \( \hat{\rho} \) via Eq. (2) not only preserves Hermiticity but also the positivity of the density matrix. The representation of Eq. (2) via a finite difference approximation
\[ \frac{\hat{\rho}(\beta + \delta \beta) - \hat{\rho}(\beta)}{\delta \beta} = -\frac{\hat{H}\hat{\rho}(\beta)}{2} - \frac{\hat{\rho}(\beta)\hat{H}}{2} + O(\delta \beta), \] (3)

where \( \delta \beta \) is a small inverse temperature increment, can be recast as
\[ \hat{\rho}_{n+1} = \left(1 - \frac{\delta \beta}{2} \hat{H}\right) \hat{\rho}_n \left(1 - \frac{\delta \beta}{2} \hat{H}\right)^\dagger + O(\delta \beta^2). \] (4)

Here, \( \hat{\rho}_n = \hat{\rho}(\beta) \) and \( \hat{\rho}_{n+1} = \hat{\rho}(\beta + \delta \beta) \). Because the r.h.s. of Eq. (4) is in the form \( A\hat{\rho}_n A^\dagger \), we know that this method also preserves the positivity of \( \hat{\rho} \) [18]. As such, we can think of this iterative method as behaving like a quantum channel modeling cooling that maps \( \hat{\rho} \) from a higher temperature state to a lower one.

In this work, we first want to apply this symmeterization idea to fermionic systems that are described by the Fermi-Dirac distribution in a non-orthonormal basis and whose statistical behavior is described by the grand canonical ensemble. In this ensemble, systems are allowed to exchange both energy and particles with their environment. For us, this means that we need to fix the value of the chemical potential \( \mu \) before applying our method, which will allow the number of electrons \( N_e \) to change.

Because we wish to consider a non-orthonormal basis, we need to introduce the overlap matrix \( S \). The overlap matrix is a square, positive-definite matrix that characterizes the overlap between the basis vectors used to describe a system. It is common to use the atomic orbital basis set so that \( S \) describes the overlap of atomic orbitals in the system. For basis vectors \( |i\rangle, |j\rangle \) the elements of the overlap matrix are given by the following expression
\[ S_{ij} = \langle i|j\rangle. \] (5)

We use \( P \) and \( H \) to denote the matrix representations of \( \hat{\rho} \) and \( \hat{H} \) respectively in the non-orthonormal basis. The elements of these matrices \( P \) and \( H \) are
\[ P_{ij} = \langle i|\hat{\rho}|j\rangle, \quad H_{ij} = \langle i|\hat{H}|j\rangle. \] (6)

Using these representations, we can obtain the following expression for the Fermi-Dirac distribution in a general basis (see Appendix A for details):
\[ P(\beta) = S \frac{1}{1 + \exp[\beta(S^{-1}H - \mu)]}, \] (7)

Note that if \( \beta = 0 \), \( P(0) = S/2 \), which we use as the initial value. The derivative of \( P \) with respect to \( \beta \) reads
\[ \frac{dP}{d\beta} = -P(1 - S^{-1}P)(S^{-1}H - \mu) \] (8)

Symmeterizing this expression and combining the result with the initial value allows us to formulate the following initial value problem:
\[ \frac{dP}{d\beta} = -P(1 - S^{-1}P)(S^{-1}H - \mu)/2 \]
\[ - (HS^{-1} - \mu)(1 - PS^{-1})P/2, \]
\[ P(0) = S/2. \] (10)

Previous works [2, 4, 5] have generally only considered systems that are described by orthogonal bases. Additionally, works [3] that have considered systems with non-orthogonal bases did so by applying a change of basis to a method that was obtained by considering systems with orthogonal bases. In contrast, we have developed our method using a version of the Fermi-Dirac distribution that is valid for systems with non-orthogonal bases. This makes our method more general without requiring additional calculations to convert \( \frac{dP}{d\beta} \) to the correct basis. Unlike the symmeterized expressions presented in [2, 4, 5], Eq. (9) is shown below to be explicitly positivity-preserving. Since these previous works were focused on obtaining the density matrix for the ground state, they made additional use of the McWeeney purification algorithm [19] to enforce idempotency on \( P \). Nevertheless, such approaches cannot be generalized to a finite temperature case.

To demonstrate that Eq. (9) explicitly preserves positivity, we proceed in an identical fashion to how we obtained Eq. (1), i.e., we first approximate Eq. (9) using the explicit Euler method and rearrange terms to obtain a algorithm for obtaining \( P_{n+1} \) from \( P_n \). The result is
\[ P_{n+1} = (1 + K_n)P_n (1 + K_n)^\dagger + O(\delta \beta^2), \] (11)
\[ K_n = -\frac{\delta \beta}{2} (HS^{-1} - \mu)(1 - P_n S^{-1}). \] (12)

Representation (11) confirms that Eq. (9) is indeed positivity-preserving.

Though Eq. (11) is only a first order scheme, it can be generalized to an arbitrarily larger order. As an example, the second-order method reads
\[ P_{n+1} = K_n P_n K_n^\dagger + A_n P_n A_n^\dagger + O(\delta \beta^3), \] (13)
\[ A_n = 1 + K_n (1 + \frac{K_n}{2}) \]
\[ + \frac{\delta \beta}{4} (HS^{-1} - \mu)(P_n K_n^\dagger + K_n P_n) S^{-1}. \] (14)

III. SUBTLETIES WITH THE CANONICAL ENSEMBLE

It is also possible to derive an initial value problem similar to Eqs. (9) and (10) that describes systems in the
canonical ensemble \[2, 5\]. In this ensemble, a system is only allowed to exchange energy with their environment, which means that \(N_e\) should remain constant as we iterate towards the desired temperature. This constraint can be enforced by updating the value of \(\mu\) with every step. Thus we now have \(\mu = \mu(\beta)\) and Eq. (7) becomes

\[
P(\beta) = N S \frac{1}{1 + \exp[\beta(S^{-1}H - \mu(\beta))]}, \tag{15}
\]

\[
N = 2N_e / \text{Tr}[S],
\]

where \(N\) is a constant term that sets \(\text{Tr}[P(0)] = N_e\). To clean up some of our future expressions, we can introduce

\[
P = (1 - S^{-1}P/N).
\]

Now our expression for \(\frac{dP}{d\beta}\) is

\[
\frac{dP}{d\beta} = -X \left( S^{-1}H - \mu - \beta \frac{d\mu}{d\beta} \right) / 2 \tag{17}
\]

\[
- \left( HS^{-1} - \beta \frac{d\mu}{d\beta} \right) X^\dagger/2. \tag{18}
\]

To insure that \(N_e\) is conserved when \(\beta\) is increasing, we solve \(\frac{dN_e}{d\beta} = \frac{d\text{Tr}[P(\beta)]}{d\beta} = 0\) for the unknown \(\mu + \beta \frac{d\mu}{d\beta}\) to obtain

\[
\mu + \beta \frac{d\mu}{d\beta} = \frac{\text{Tr}[XS^{-1}H + HS^{-1}X^\dagger]}{\text{Tr}[X + X^\dagger]}.
\]

To construct the sought initial value problem

\[
\frac{dP}{d\beta} = -\frac{X}{2} \left( S^{-1}H - \frac{\text{Tr}[XS^{-1}H + HS^{-1}X^\dagger]}{\text{Tr}[X + X^\dagger]} \right) \tag{20}
\]

\[
- \left( HS^{-1} - \frac{\text{Tr}[XS^{-1}H + HS^{-1}X^\dagger]}{\text{Tr}[X + X^\dagger]} \right) X^\dagger/2,
\]

\[
P(0) = \frac{NS}{2}. \tag{21}
\]

By solving this initial value problem, we can calculate \(P(\beta)\) while ensuring that \(N_e\) is conserved. Note that Eq. (20) is also positivity-preserving by construction.

Sometimes, it is also useful to know the value of the chemical potential \(\mu\) for the system at a given temperature. This can be achieved by solving the initial value problem

\[
\frac{d\mu}{d\beta} = \frac{1}{\beta} \left( \frac{\text{Tr}[XS^{-1}H + HS^{-1}X^\dagger]}{\text{Tr}[X + X^\dagger]} - \mu \right), \tag{22}
\]

\[
\mu(0) = \frac{\text{Tr}[H]}{\text{Tr}[S]}. \tag{23}
\]

in conjunction with Eqs. (20) and (21). Equation (22) directly follows from Eq. (19).

A review of previous works in DMM methods reveals that the presence of \(\frac{d\mu}{d\beta}\) in Eq. (17) appears to be an overlooked subtlety. The previous methods that explicitly preserve \(N_e\) \[2, 5\] make no mention of the importance of calculating \(\frac{d\mu}{d\beta}\) to obtain the correct value of \(\mu\), while others \[3, 4\] focus on the grand canonical ensemble and only refer to the fact that conserving \(\mu\) is easier than conserving \(N_e\). To the best of our knowledge, our handling of the canonical ensemble is the first to correctly account for the presence of \(\frac{d\mu}{d\beta}\) in Eq. (17).

IV. NON-LINEARITY IN THE HAMILTONIAN

Throughout our discussion so far, we have implicitly assumed that \(H\) is independent of \(\beta\). To account for electron-electron interactions, the Hamiltonian is usually represented as

\[
H = H_{\text{core}} + H_{\text{exc}}(P), \tag{24}
\]

where the correction \(H_{\text{exc}}(P)\), depending on the sought density matrix \(P\), is typically obtained within the density functional theory \[20, 21\].

Note that one needs to be careful in formulating an initial value problem if \(H_{\text{exc}}\) is included. Since in that case, \(H\) starts depending on \(\beta\) and generally speaking \([H, \frac{dH}{d\beta}] \neq 0\). This implies that the order of matrices in the expression for \(\frac{dP}{d\beta}\) matters. In Ref. \[22\], it has been established that

\[
\frac{d}{d\beta} e^{\beta h} = e^{\beta h} \frac{d}{d\beta} \int_0^\beta e^{-(\beta-x)h} \frac{d}{dx} e^{-xh} dx, \tag{25}
\]

\[h = S^{-1}H(\beta) - \mu.\]

To obtain more accurate methods, the integral in Eq. (25) needs to be accounted for. To the best of our knowledge, this term has been omitted in preceding works.

V. ILLUSTRATIONS

A. Hückel Theory Model

The Hückel theory serves as a useful benchmark for many methods of solving problems concerning electronic structure, as it is a simple method for determining the energies of the orbitals of \(\pi\)-electrons \[23, 24\]. The Hamiltonian used in Hückel theory is a tight-binding 1D chain with \(\alpha\) along the main diagonal to describe the on-site energy and \(\gamma\) along the first diagonals above and below the main diagonal to describe the nearest-neighbor energy. This chain is made infinite by imposing the periodic boundary condition: \(H_{1N} = H_{N1} = \gamma\). In this work, we consider a Hamiltonian with \(N = 50\) at half-filling (\(N_e = 25\)) with \(\alpha = 0.569\) and \(\gamma = 0.066\). For the grand canonical method, we solve Eqs. (9) and (10) using a value for \(\mu\) that is the average of the two middle eigenvalues of \(H\). For the canonical method, we solve Eqs. (20) and (21) while simultaneously solving Eqs. (22) and (23).
FIG. 1. Eigenvalue spectra of a) the exact matrix obtained by calculating Eq. (7) and the matrix obtained by solving Eqs. (9) and (10); b) the exact matrix obtained by calculating Eq. (15) and the matrix obtained by solving Eqs. (20) and (21) for a system with a Hückel theory Hamiltonian. In each case, the eigenvalues of our results coincide with the exact eigenvalues, which demonstrates the effectiveness of our methods for a linear system described by an orthogonal basis.

FIG. 2. Eigenvalue spectra of a) the exact matrix obtained by calculating Eq. (7) and the matrix obtained by solving Eqs. (9) and (10); b) the exact matrix obtained by calculating Eq. (15) and the matrix obtained by solving Eqs. (20) and (21) for HF when considering only the core Hamiltonian. To make each point visible, we chose to plot the spectra against their index. In each case, the spectra of our results demonstrate strong agreement with the exact values, which indicates the ability of our methods to handle systems with non-orthogonal bases.

to update the value of $\mu$. Both the grand canonical and canonical methods were implemented using the fourth-order Runge-Kutta method with $\beta = 300$ as our stopping point and a step-size $\delta \beta = 0.03$. All the codes used can be accessed in [25]. The resulting eigenvalue spectra of the density matrix $P$ in each case is displayed in Fig. 1.

B. Hydrogen Fluoride

For our second demonstration, we chose to use HF due to its relative simplicity despite being represented in an non-orthogonal basis and described by a non-linear (i.e., density functional theory) Hamiltonian [24]. To test the ability of our methods to handle systems described by general bases, we first considered only the core Hamiltonian ($H_{\text{core}}$). The PySCF library [26] was used to obtain $H_{\text{core}}$ and the overlap matrix $S$ for this system. The results of our grand canonical method were obtained by solving Eqs. (9) and (10) with $\mu$ given by the average of the middle two eigenvalues of $H_{\text{core}}$. The results of our canonical method were obtained by solving Eqs. (20) and (21) while simultaneously solving Eqs. (22) and (23) to update the value of $\mu$. Both of our methods were implemented using the fourth-order Runge-Kutta method with final value $\beta = 3$ and step-size $\delta \beta = 0.003$ [25]. In Fig. 2, the eigenvalue spectra of our results are compared to the eigenvalue spectra obtained by directly calculating $P$ from Eq. (7) for the grand canonical ensemble or Eq. (15) for the canonical ensemble. In each case, the obtained populations coincide with the exact values, which demonstrates the effectiveness of methods [9]-[10].
and Eqs. (20)–(21) in calculating the density matrix for electronic systems at finite temperatures that are described by a non-orthogonal basis.

In our third and final demonstration, we include the non-linearities in the Hamiltonian for HF by modifying our methods to calculate \( H \) according to Eq. (24) using the current \( P \). This is performed at the beginning of each step in both of our methods and is accomplished through the use of the PySCF library [26]. For our grand canonical method, we again set \( \mu \) equal to the average of \( H_{\text{core}} \)'s middle two eigenvalues and evolve Eqs. (9) and (10). For our canonical method, we use Eqs. (20) and (21) while simultaneously solving Eqs. (22) and (23) to update \( \mu \). In both methods, we employed the fourth-order Runge-Kutta method with a final value \( \beta = 3 \) and a step-size \( \delta \beta = 0.003 \). When calculating the exact results, it is necessary to account for the non-linearities in \( H \). This is done in a self-consistent manner for the grand canonical ensemble by swapping in Eqs. (21) and (15) for Eqs. (10) and (7). We found that the rate of convergence for these calculations can be improved using the Aitken’s delta-squared process [27]. The eigenvalue spectra for the results of our methods and the exact results are displayed in Fig. 3. In both ensembles, our methods achieved similar results to their corresponding exact values, though there are deviations. We believe that these deviations arise because we neglected to account for \( \delta \beta \neq 0 \) as described in Sec. IV. This explanation is further supported by the fact that the grand canonical method obtained results that matches the corresponding exact results better than the canonical method, which uses \( H \) to update \( \mu \) for each step.

VI. CONCLUSION

We have developed positivity-preserving methods for calculating the Fermi-Dirac density matrices at finite temperatures for both the canonical (Sec. III) and grand canonical (Sec. IV) ensembles. These methods model a physical process of cooling a state initially at infinite temperature down to the temperature of interest. This approach may lay the ground for a new generation of DMM methods. A possible future direction is to utilize the fact that a low-temperature Fermi-Dirac density matrix is of a low rank, hence it is possible to further accelerate calculations by utilizing low-rank corner space techniques recently developed for solving master equations for large open quantum systems [28–32].

Appendix A: Non-Orthonormal Fermi-Dirac

We want to derive an expression for the Fermi-Dirac distribution that is valid for a general, non-orthonormal basis. Consider the general, non-orthonormal basis set: \( \{|i\rangle\}_{i=0}^{N} \) where \( N \) is the dimensionality of the system in question. Let \( S = (\langle ij|) \) be the definition of the overlap matrix, let \( \hat{H} \) be the Hamiltonian operator, and let \( \hat{\rho} \) be the Fermi-Dirac distribution

\[
\hat{\rho}(\beta) = \frac{1}{1 + \exp[\beta(\hat{H} - \mu)]}.
\]

Now let \( P = (\langle i|\hat{\rho}|j\rangle) \), \( H = (\langle i|\hat{H}|j\rangle) \) be the representations of \( \hat{\rho} \) and \( \hat{H} \) in the non-orthonormal basis respectively. Then the Taylor Series expansion for \( \hat{\rho} \) reads

\[
P = \sum_{n=0}^{\infty} a_n \langle i|\hat{A}^n|j\rangle,
\]

where \( \hat{A} = (\hat{H} - \mu) \) and has the representation \( A = (\langle i|\hat{A}|j\rangle) \) in the non-orthonormal basis. The goal is to find the representation of \( \langle i|\hat{A}^n|j\rangle \) in the non-orthonormal basis so that we can obtain a concise expression for \( P \). We
start by considering how $\hat{A}$ acts on a basis vector $|j\rangle$. If we expand $|j\rangle$ in the basis $\{|k\rangle\}$, we get

$$
\langle i|\hat{A}|j\rangle = \langle i| \sum_k C_{kj}|k\rangle = \sum_k C_{kj} \langle i|k\rangle = SC
$$

(A3)

where $C = S^{-1}A$ is just the matrix of coefficients obtained from $\hat{A}|j\rangle$. We can perform similar expansions to obtain $\langle i|\hat{A}^n|j\rangle$ for $n > 1$ and then use induction to show that

$$
\langle i|\hat{A}^n|j\rangle = A(S^{-1}A)^{n-1}.
$$

(A4)

If we multiply both sides of Eq. (A2) by $S^{-1}$ on the left and substitute in for $\langle i|\hat{A}^n|j\rangle$, we obtain

$$
S^{-1}P = \sum_{n=0}^{\infty} a_n(S^{-1}A)^n = \frac{1}{1 + \exp[1/\beta(S^{-1}A)]},
$$

(A5)

Finally, we replace $A$ with $\langle i| (\hat{H} - \mu)|j\rangle$ and solve for $P$ to obtain

$$
P = S \frac{1}{1 + \exp[1/\beta(S^{-1}H - \mu)]}.
$$

(A6)

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