

## Density-matrix functional method for electronic properties of impurities

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We develop a density-matrix correlation-energy functional suitable for treating impurity sites with strong electronic correlations. The functional is based on a rigorous theorem about the form of such functionals as well as an exact inequality for the exchange-correlation energy. It is validated by comparison with exact results for small clusters, and is used to treat the electronic properties of an Anderson impurity in a random alloy.

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### I. INTRODUCTION

Most existing methods for calculating the electronic ground state of molecules and solids, such as Hartree-Fock theory and existing implementations of density-functional theory, have difficulties describing strongly correlated electronic systems. More complete treatments of correlations are available but have very unfavorable system-size scaling. These difficulties have sparked recent interest in density-matrix functionals,<sup>1-7</sup> in which the exchange and correlation energies are given in terms of the electronic density matrix rather than just the charge density. The general theory of such methods is given in Refs. 1-3 and some preliminary implementations have been given in Refs. 4-7. However, the specific implementations presented to date either suffer from serious inaccuracies in important test cases or have a very limited range of applications.

In this paper, we develop a density-matrix functional method that treats a broad range of impurity models with high accuracy. The goal of this method is to obtain accurate estimates of key ground-state quantities such as on-site charges and fluctuations, rather than treating subtle many-body phenomena such as the Kondo effect in the Anderson model.<sup>8</sup> The method is based on two exact results that we will introduce in Sec. II. The first concerns the general mathematical form of the electron interaction energy in terms of the density matrix. The second is an inequality relating the interaction energy to a simple moment of the density matrix. The accuracy of the method is evaluated for simple model Hamiltonians by comparison with exact results (Sec. III). Finally, in Sec. IV we use this approximation to investigate the combined effects of electron interactions and disorder for Anderson impurities in random alloys.

We emphasize that the present approach is distinct from recent applications of density matrices to  $\mathcal{O}(N)$  implementations of density-functional theory.<sup>9-11</sup> These implementations employ standard exchange-correlation functionals and attempt to achieve idempotency in the density matrix; the physical density matrix (and that obtained here) has eigenvalues between zero and one. Our approach is also unrelated to density-matrix renormalization-group theory<sup>12,13</sup> and two-particle density matrix theory,<sup>14-16</sup> based on the contracted Schrödinger equation.<sup>17,18</sup>

### II. DENSITY MATRIX FUNCTIONAL

We treat systems described by tight-binding Hamiltonians of the form

$$\mathcal{H} = \sum_{ij} h_{ij} \hat{c}_i^\dagger \hat{c}_j + \frac{1}{2} \sum_{i,j,k,l \in \mathcal{S}} U_{ijkl} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k, \quad (1)$$

where  $i, j, k$ , and  $l$  are spin-orbital indices and  $\mathcal{S}$  is a subspace of the Hilbert space. Physically this would correspond to a system for which the strongest electron interactions are restricted to the orbitals in  $\mathcal{S}$ . The energy expectation value for an  $N$ -body wave function  $|\Psi\rangle$ ,  $\langle \mathcal{H} \rangle$ , is completely determined by the one-body density matrix  $\hat{\rho}$ , defined by  $\rho_{ij} = \langle \hat{c}_i^\dagger \hat{c}_j \rangle$ , and the interaction energy  $E_{\text{int}} = \sum U_{ijkl} \langle \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k \rangle$ . Following Levy's approach,<sup>3</sup> we define  $E_{\text{int}}[\hat{\rho}]$  as the minimum of  $E_{\text{int}}$  over all wave functions  $|\Psi\rangle$  that yield the same density matrix  $\hat{\rho}$ . For the ground-state density matrix  $\hat{\rho}$ ,  $E_{\text{int}}[\hat{\rho}]$  is the physically correct value of the interaction energy.

The first result we prove is that  $E_{\text{int}}[\hat{\rho}]$  is completely determined by the local moments of  $\hat{\rho}$  in the subspace  $\mathcal{S}$ :

$$E_{\text{int}}[\hat{\rho}] = E_{\text{int}}[\hat{\rho}_{\mathcal{S}}, \hat{\rho}_{\mathcal{S}}^{(2)}, \hat{\rho}_{\mathcal{S}}^{(3)} \dots], \quad (2)$$

where  $\hat{\rho}_{\mathcal{S}}^{(n)}$  is the restriction of  $\hat{\rho}^n$  to  $\mathcal{S}$ . This result will motivate our form for the correlation-energy functional. To prove it, we introduce a unitary matrix  $R$  that leaves the subspace  $\mathcal{S}$  invariant and a corresponding unitary operator  $\mathcal{R}$  that acts on the many-body wave function  $|\Psi\rangle$ . It is defined by

$$\mathcal{R} \prod_{\varphi} \hat{c}_{\varphi}^{\dagger} |0\rangle = \prod_{\varphi} \hat{c}_{R\varphi}^{\dagger} |0\rangle, \quad (3)$$

where the  $\varphi$  are any one-electron basis orbitals. We first note that

$$E_{\text{int}}[R^{\dagger} \hat{\rho} R] = E_{\text{int}}[\hat{\rho}]. \quad (4)$$

It is simple to show that the density matrix of  $\mathcal{R}|\Psi\rangle$  is given by  $R^{\dagger} \hat{\rho} R$ ;  $\mathcal{R}|\Psi\rangle$  also has the same value of  $E_{\text{int}}$  as  $|\Psi\rangle$  since  $\mathcal{R}$  commutes with any  $\hat{c}_i^{\dagger}$ ,  $|i\rangle \in \mathcal{S}$ . Furthermore, if  $\mathcal{R}|\Psi\rangle$  did not have the lowest value of  $E_{\text{int}}$  given the density matrix  $R^{\dagger} \hat{\rho} R$ , one could backtransform to the original density matrix to obtain a lower  $E_{\text{int}}$  for the original problem. Thus Eq. (4) holds. Now consider two density matrices  $\hat{\rho}_1$  and  $\hat{\rho}_2$  that have equal values of all of the moments  $\hat{\rho}_{\mathcal{S}}^{(n)}$ ; in other words,  $\langle i | \hat{\rho}_1^n | j \rangle = \langle i | \hat{\rho}_2^n | j \rangle$  for all  $|i\rangle, |j\rangle \in \mathcal{S}$ . It is straightforward to

show<sup>21</sup> that  $\hat{\rho}_1$  and  $\hat{\rho}_2$  are then related by a unitary transformation  $R$  of the underlying vector space, and this transformation leaves all  $|i\rangle \in \mathcal{S}$  invariant.<sup>19</sup> Therefore,  $E_{\text{int}}[\hat{\rho}_1] = E_{\text{int}}[\hat{\rho}_2]$ , and Eq. (2) follows.

We next derive a class of inequalities for  $E_{\text{int}}[\hat{\rho}]$  for the special case of a two-dimensional subspace  $\mathcal{S}$  spanned by orbitals  $|i\rangle$  and  $|j\rangle$ , and show that the tightest inequalities of this class are given by the second moments of the density matrix  $\rho_{ii}^{(2)} = \langle i|\hat{\rho}^2|i\rangle$  and  $\rho_{jj}^{(2)} = \langle j|\hat{\rho}^2|j\rangle$ . We define  $U = U_{ijij}$  and  $E_{\text{int}} = UP$ , where  $P = \langle \hat{n}_i \hat{n}_j \rangle$ . We first note that  $|\Psi\rangle$  can always be decomposed into four pieces corresponding to the occupancies of the orbitals  $|i\rangle$  and  $|j\rangle$ :

$$|\Psi\rangle = \omega_0|\Phi_0\rangle + \omega_i \hat{c}_i^\dagger |\Phi_i\rangle + \omega_j \hat{c}_j^\dagger |\Phi_j\rangle + \omega_{ij} \hat{c}_i^\dagger \hat{c}_j^\dagger |\Phi_{ij}\rangle. \quad (5)$$

The many-body wave functions  $|\Psi\rangle$  and  $|\Phi_{\dots}\rangle$  are taken to be normalized, and the wave functions  $|\Phi_{\dots}\rangle$  do not contain the orbitals  $|i\rangle$  and  $|j\rangle$ . Using this decomposition, the density-matrix element connecting the one-particle state  $|i\rangle$  and an arbitrary one-particle state  $|\mu\rangle$  orthogonal to  $\mathcal{S}$  is given by

$$\begin{aligned} \rho_{i\mu} &= \langle \Psi | \hat{c}_i^\dagger \hat{c}_\mu | \Psi \rangle \\ &= \omega_i \omega_0 \underbrace{\langle \Phi_i | \hat{c}_\mu | \Phi_0 \rangle}_{M_1} + \omega_{ij} \omega_j \underbrace{\langle \Phi_{ij} | \hat{c}_\mu | \Phi_j \rangle}_{M_2}. \end{aligned} \quad (6)$$

The matrix elements  $|M_1|$  and  $|M_2|$  are bounded by unity, so using the Schwartz inequality yields for any  $|\mu\rangle$

$$|\rho_{i\mu}| \leq f(P, n_i, n_j), \quad (7)$$

with

$$f(P, n_i, n_j) = \underbrace{\sqrt{(n_i - P)(1 - n_i - n_j + P)}}_{|\omega_i \omega_0|} + \underbrace{\sqrt{P(n_j - P)}}_{|\omega_{ij} \omega_j|}, \quad (8)$$

where we have expressed the  $\omega$ 's in terms of the occupancies of states  $|i\rangle$  and  $|j\rangle$ ,  $n_i = \rho_{ii}$ , and  $n_j = \rho_{jj}$ , respectively, as well as in terms of  $P = \langle \hat{n}_i \hat{n}_j \rangle$ . A similar inequality holds for  $\rho_{j\mu}$ :

$$|\rho_{j\mu}| \leq f(P, n_j, n_i). \quad (9)$$

Since the right-hand side of the inequality equation (7) is independent of  $|\mu\rangle$ , the tightest inequality is obtained if we choose the state  $|\mu\rangle$  to maximize  $\rho_{i\mu}$ , which occurs for

$$|\mu\rangle = \sum_{\alpha \neq i, j} \rho_{i\alpha} |\alpha\rangle / \sqrt{\sum_{\alpha \neq i, j} \rho_{i\alpha}^2}. \quad (10)$$

Then

$$\rho_{i\mu} = \sqrt{\sum_{\alpha \neq i, j} \rho_{i\alpha}^2} = \sqrt{\rho_{ii}^{(2)} - \rho_{ii}^2 - \rho_{ij}^2}. \quad (11)$$

Thus, the tightest inequality of the type as in Eq. (7) is based on the second moment of the density matrix  $\rho_{ii}^{(2)}$ .

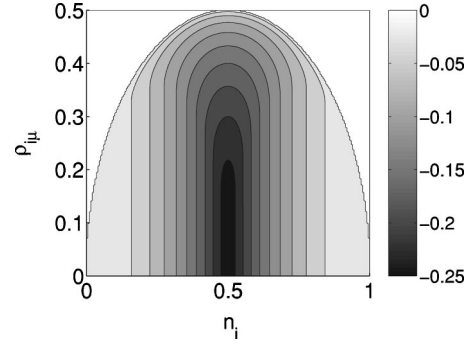


FIG. 1. Graphical representation of the inequality equation (7) for  $P = \langle n_i n_j \rangle$  showing the lower bound of the correlation  $\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle$  as a function of  $n_i$  and  $\rho_{i\mu}$  for the case  $n_i = n_j$ .

The inequality provides both lower and upper bounds for  $P$ . We use the lower bound for the  $U > 0$  case of interest here. Figure 1 plots the lower bound of the correlation  $\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle$  as a function of  $\rho_{i\mu}$  and  $n_i$  for the case  $n_i = n_j$ . At the upper limit for  $\rho_{i\mu}$ ,  $\rho_{i\mu} = \sqrt{n_i(1 - 2n_i)}$ , the correlation is zero corresponding to the Hartree-Fock limit. Decreasing values of the off-diagonal term  $\rho_{i\mu}$  lead to lower values of  $P$ , i.e., stronger correlations. The effect is most evident for half-filling. The largest correlations occur for  $\rho_{i\mu} = 0$ , where in fact  $P = 0$  in the range  $0 < n_i < 1/2$ .

We use the lower bound for  $P[\hat{\rho}]$  as an approximation to the exchange-correlation functional and call it the second-moment approximation.<sup>20</sup> It corresponds to keeping only the first two arguments of  $E_{\text{int}}$  on the right-hand side of Eq. (2). For a given density matrix and a positive (negative)  $U$ ,  $P[\hat{\rho}]$  is approximated as the smallest (largest)  $P$  obeying the constraints of the inequalities for  $\rho_{i\mu}$  and  $\rho_{j\mu}$  [cf. Eqs. (7) and (9)]. For repulsive interactions ( $U > 0$ ) we thus define the interaction energy  $E_{\text{int}}$  as

$$E_{\text{int}} = UP_{\text{min}}, \quad (12)$$

where

$$\begin{aligned} P_{\text{min}} &= \inf [P | \rho_{i\mu} \leq f(P, n_i, n_j) \wedge \\ &\quad \times \rho_{j\mu} \leq f(P, n_j, n_i) \wedge 0 \leq P \leq n_i n_j], \end{aligned} \quad (13)$$

and  $f$  and  $\rho_{i\mu}$  are given by Eqs. (8) and (11), respectively. For practical implementation we first check if the lowest possible value for  $P$ , i.e.,  $P = 0$ , fulfills the inequalities. In this case  $P_{\text{min}} = 0$ . Otherwise  $P_{\text{min}}$  is given by the larger of the two solutions for  $P$  of the inequalities in Eqs. (7) and (9) used as equalities.

### III. ACCURACY OF THE FUNCTIONAL

We have shown analytically<sup>21</sup> that the second-moment approximation yields the exact ground state for a heteropolar dimer molecule with arbitrary on-site Coulomb interactions and that for fluctuating-dipole interactions the results are in agreement with second-order perturbation theory, even when intersite electronic couplings are present.

For more complex models of the form of Eq. (1), we implement the second-moment approximation as a varia-

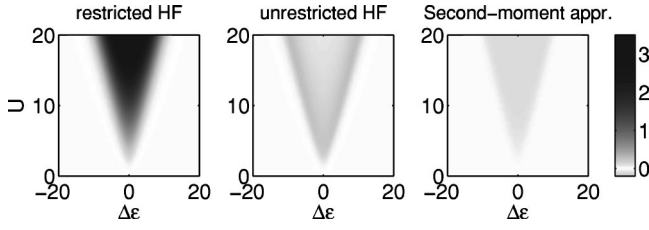


FIG. 2. Error in the total energy of a six-site Anderson chain with six electrons and spin zero in different approximations: restricted Hartree-Fock (left), unrestricted Hartree-Fock (center), and second-moment approximation (right). The energy unit is  $h$ , cf. Eq. (14).

tional method. The density matrix is written as  $\hat{\rho} = O \Lambda O^\dagger$  using an orthogonal matrix  $O$  and a vector of occupation numbers  $\Lambda$ . To ensure ensemble  $N$  representability<sup>2,22</sup> of the density matrix  $\hat{\rho}$ , the eigenvalues  $\Lambda_i$  are constrained to be between zero and one. The energy minimization of the density matrix uses a conjugate gradient routine. The gradient is calculated under the constraint of orthonormal natural orbitals following the idea presented in Ref. 23. The total number of up and down spin electrons is fixed by a penalty function. The running time of the implemented algorithm is  $\mathcal{O}(N^3)$  and the memory usage  $\mathcal{O}(N^2)$ . Calculations for Anderson-type chains of up to 100 sites have been performed.

To test the accuracy of the second-moment approximation, we perform calculations for short Anderson chain models using the Hamiltonian

$$\mathcal{H} = (\Delta\epsilon - U/2) \sum_{\sigma} \hat{c}_{0\sigma}^\dagger \hat{c}_{0\sigma} - h \sum_{(ij)\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \hat{n}_{0\uparrow} \hat{n}_{0\downarrow}, \quad (14)$$

where the second sum is over nearest neighbor sites only. The results for a six-site Anderson chain are compared to exact diagonalization of the many-body Hamiltonian as well as to restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) theory. Figure 2 shows the error in the total energy. The absence of correlation in RHF leads to a substantial overestimate of the energy. The UHF approximation recovers part of the correlation energy by developing a permanent local moment on the interaction site for large  $U$  and small  $|\Delta\epsilon|$ . For smaller  $U$  and away from half-filling, i.e., large  $|\Delta\epsilon|$ , no moment is formed and thus no correlation energy is obtained by UHF. The second moment approximation, on the other hand, is in close overall agreement with the exact results. It slightly overestimates the correlation energy with a maximum error of 20% for intermediate  $U$  and half-filled sites.

Figure 3(a) shows the impurity site occupancy  $n_0$  vs  $\Delta\epsilon$  for a strongly interacting case in the second-moment approximation, RHF, and UHF, compared to exact results. The impurity occupancy decreases stepwise with increasing  $\Delta\epsilon$ . The steps become sharper as  $U$  increases. RHF obtains no stepwise behavior at all. The UHF approximation improves on this by formation of a local moment, but shows a cusp. The second-moment approximation, on the other hand, describes the charge of the impurity very accurately. Similar accuracy is obtained for the spin fluctuations of the impurity.

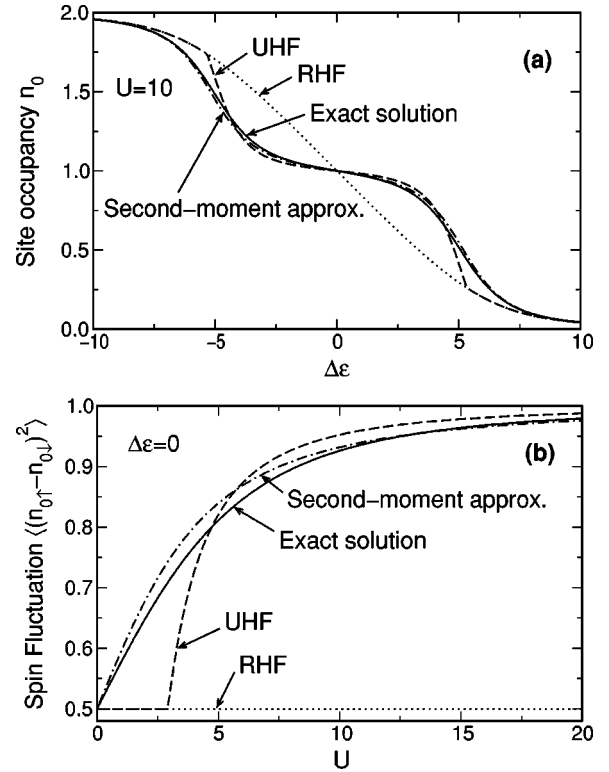


FIG. 3. Site occupancy (a) and spin fluctuations (b) on the interaction site for a six-site Anderson chain with six electrons and spin zero.

Figure 3(b) shows results for these fluctuations in the symmetric case ( $\Delta\epsilon=0$ ). In agreement with the exact result, the spin fluctuations in the second-moment approximation increase gradually from  $1/2$  to  $1$  with increasing  $U$ . The UHF results show no enhancement at all for small  $U$ , but “catch up” for larger  $U$ . RHF gives no enhancement whatsoever.

For Hubbard chain models with on-site interactions on all sites, our numerical studies<sup>21</sup> show that the second-moment approximation is less accurate. The magnitude of the error in energy is comparable to the error of the unrestricted Hartree-Fock approximation. This result is not surprising since the approximation was derived using the assumption of only two interacting orbitals.

Altogether the second-moment approximation provides an accurate treatment of on-site correlations on isolated impurity sites and at the same time has adequate computational efficiency to treat realistic electronic structures.

#### IV. ANDERSON IMPURITY IN A RANDOM ALLOY

We now demonstrate the utility of our method by addressing the problem of an Anderson impurity in a random alloy. The heart of this problem is the competition or cooperation between the electron-electron interactions and the disorder, and to our knowledge this physics has not been addressed by calculations to date. We expect that the coupling of the impurity to the host will be reduced by both disorder and electron interactions. However, the disorder and interaction effects on spin fluctuations should oppose each other. The

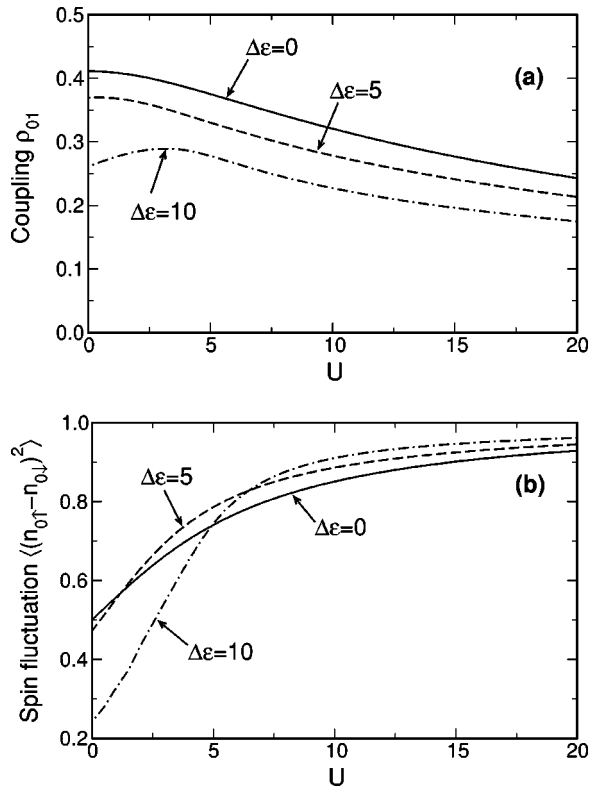


FIG. 4. Anderson impurity in a disordered alloy: coupling between the impurity and the bulk (a) and spin fluctuations on the impurity site (b).

disorder tends to favor either zero or double occupancy, whereas the interactions favor single occupancy and thus enhance spin fluctuations.

We use a simple cubic underlying lattice with random on-site potentials  $\epsilon_i = \pm \Delta\epsilon/2$  (except at the impurity site) at half-filling. We employ the recursion method<sup>24</sup> to transform

the one-body Hamiltonian to a chain of length 20 and average over 50 alloy configurations. We evaluate the properties of the impurity as a function of the Coulomb interaction  $U$  for different disorder potentials  $\Delta\epsilon = 0, 5h, 10h$ . The coupling between the impurity and the bulk is reduced by both disorder and Coulomb interactions as seen in Fig. 4(a). The spin fluctuations at small  $U$  are reduced by the disorder [cf. Fig. 4(b)], as expected from the above arguments based on site occupancy. However, for larger values of  $U$ , the disorder enhances the spin fluctuations. The crossover value of  $U$  depends on  $\Delta\epsilon$  and is about  $5h$  for  $\Delta\epsilon = 10h$ . At large  $U$ , the impurity is essentially always half-filled, and the reduced couplings between the impurity and the environment lead to the enhancement.

## V. CONCLUSION

In summary, we have shown that for a large class of impurity model Hamiltonians the exchange-correlation energy is determined entirely by the local moments of the density matrix. An exact inequality relates the second moment of the density matrix with the correlation energy. This inequality, used as an approximation to the correlation energy, gives very accurate results for the energy, one-electron properties and charge and spin fluctuations of Anderson impurities. Application of the method to an Anderson impurity in a random alloy has revealed an unexpected crossover behavior in the effects of disorder and electron interactions on the spin fluctuations. Future work should aim at the extension of the approximation to systems with more interacting orbitals, so that a broader range of systems can be treated.

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<sup>19</sup>This result holds strictly only if the vector space spanned by the set of vectors  $\hat{\rho}_{1,2}^{(n)}|i\rangle$ ,  $|i\rangle \in \mathcal{S}$  is the whole one-particle Hilbert space. If this vector space is a subspace of the one-particle Hilbert space, then  $E_{\text{im}}[\hat{\rho}_{1,2}]$  only depends on  $\hat{\rho}_{1,2}$  restricted to that subspace and we can restrict our one-particle Hilbert space to that subspace.

<sup>20</sup>Our usage of that term is distinct from the ‘‘second-moment approximation’’ used to generate semi-classical force fields (see Ref. 25). These treat noninteracting electrons and use the second moment of the Hamiltonian, not the density matrix.

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