

Supplementary material for the manuscript
“The description of strong correlation within self-consistent Green’s function
second-order perturbation theory”

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I. IMPLEMENTATION OF GF2

The GF2 algorithm is defined by the following three self-consistent equations:

$$\mathbf{G}(\omega) = [(\mu + \omega)\mathbf{S} - \mathbf{F} - \mathbf{\Sigma}(\omega)]^{-1} \quad (1)$$

$$F_{ij} = h_{ij} + \sum_{kl} P_{kl} (v_{ijkl} - \frac{1}{2} v_{iklj}) \quad (2)$$

$$\Sigma_{ij}(\tau) = - \sum_{klmnpq} G_{kl}(\tau) G_{mn}(\tau) G_{pq}(-\tau) v_{imqk} (2v_{lpnj} - v_{nplj}), \quad (3)$$

The iterative solution of the Dyson equation according to Equations 1, 2, and 3 proceeds as follows:

1. Perform a restricted Hartree-Fock calculation, obtaining the HF Fock matrix \mathbf{F}_{HF} , density matrix \mathbf{P}_{HF} , and overlap matrix \mathbf{S} .
2. Build $\mathbf{G}(\omega)$ according to Eq. 1. Assuming a Hartree-Fock reference, at first iteration $\mathbf{F} = \mathbf{F}_{\text{HF}}$, and $\mathbf{\Sigma}(\omega) = \mathbf{0}$.
 - 2.a Find μ such that $\mathbf{P}(\mathbf{G})$ has correct electron number.
 - 2.b Rebuild $\mathbf{F}(\mathbf{P})$ according to Eq. 2, and update $\mathbf{G}(\omega)$. Repeat **2.a-2.b** until $\mathbf{G}(\omega)$, \mathbf{F} , and μ are self-consistent. FFT $\mathbf{G}(\omega) \rightarrow \mathbf{G}(\tau)$.
3. Build $\mathbf{\Sigma}(\tau)$ according to Eq. 3. FFT $\mathbf{\Sigma}(\tau) \rightarrow \mathbf{\Sigma}(\omega)$. Go to step 2 and repeat until convergence.

A cartoon showing a bird's-eye view of our implementation of the GF2 algorithm is presented in Figure 1. To begin the calculation we set the chemical potential μ in the middle of the HF HOMO-LUMO gap. In subsequent iterations μ will need to be adjusted in step **2.a**, and we find that a simple bisection routine works fine for this.

Now we comment on the convergence properties of the GF2 algorithm. In cases where the system is essentially single-reference iterating to convergence is straightforward and one may allow

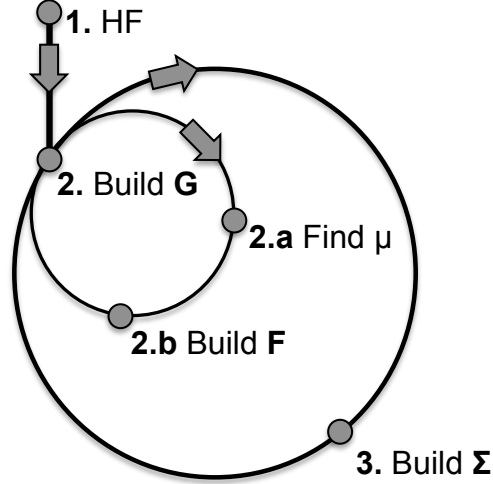


FIG. 1. A bird's-eye view of the GF2 algorithm.

loose self-consistency requirements on $\mathbf{G}(\omega)$, \mathbf{F} , and μ during the inner-loop in order to accelerate the calculation. In multi-reference cases however we find that applying tighter convergence criteria on $\mathbf{G}(\omega)$, \mathbf{F} , and μ while damping \mathbf{P} can stabilize convergence of the entire GF2 calculation. For the outer loop we find it useful to apply damping to $\Sigma(\tau)$, with the amount of damping depending on how multireference the system is.

II. ENERGY AND DENSITY MATRIX EVALUATION

Given a Green's function $\mathbf{G}(\omega)$ built from Eq. 1, we evaluate the single-particle density matrix \mathbf{P} by performing a Fourier transform of the Green's function on the imaginary frequency axis

$$G_{kl}(\tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} G_{kl}(\omega_n) e^{-\omega_n \tau}, \quad (4)$$

yielding the Green's function of imaginary time τ . This transform only needs to be performed for a single point $\tau = \beta$ since

$$\mathbf{G}(\tau = \beta) = -\frac{1}{2}\mathbf{P}, \quad (5)$$

where \mathbf{P} is the density matrix. It's important to note that the chemical potential μ in Eq. 1 will need to be adjusted iteration to iteration, to ensure that $\text{Tr}[\mathbf{P}\mathbf{S}] = N_e$, where N_e is the electron number.

There are several approaches such as the Luttinger–Ward and Klein functional or the Galitskii–

Migdal formula that can be used for evaluating the electronic energy. At self-consistency the energy obtained from all these approaches should be equal. We evaluate the electronic energy according to the Galitskii–Migdal (GM) formula that can be explicitly written as

$$E_{GM} = - \sum_{ij} G_{ij}(\tau = \beta)(2h_{ij} + \Sigma_{\infty ij}) + \frac{2}{\beta} \sum_{n=-\infty}^{\infty} \sum_{kl} [\text{Re}(G_{kl}(\omega_n))\text{Re}(\Sigma_{kl}(\omega_n)) - \text{Im}(G_{kl}(\omega_n))\text{Im}(\Sigma_{kl}(\omega_n))] . \quad (6)$$

III. PLOTS OF NATURAL OCCUPATION NUMBERS

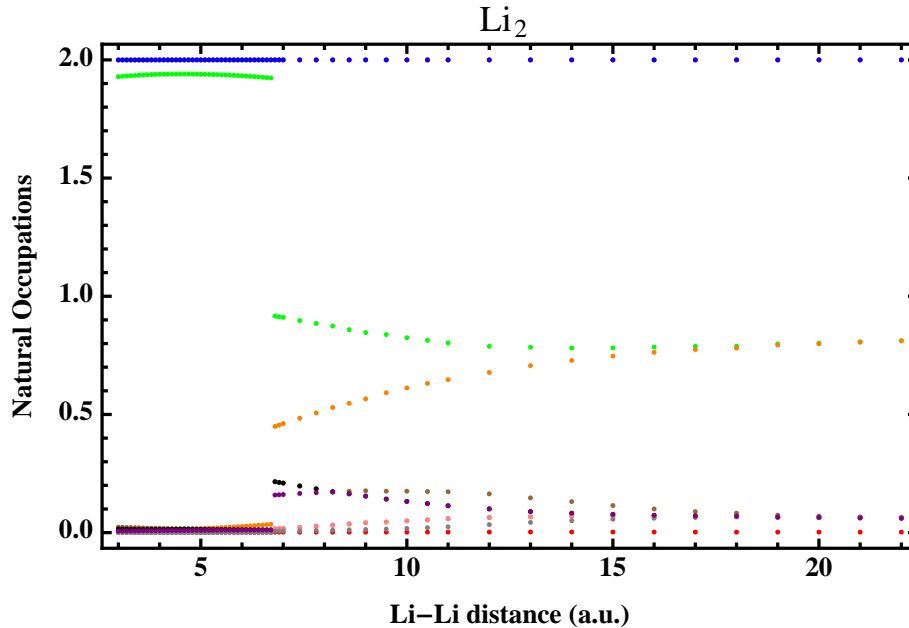


FIG. 2. Natural occupation numbers of Li₂ as calculated by GF2 with respect to Li-Li bond distance.

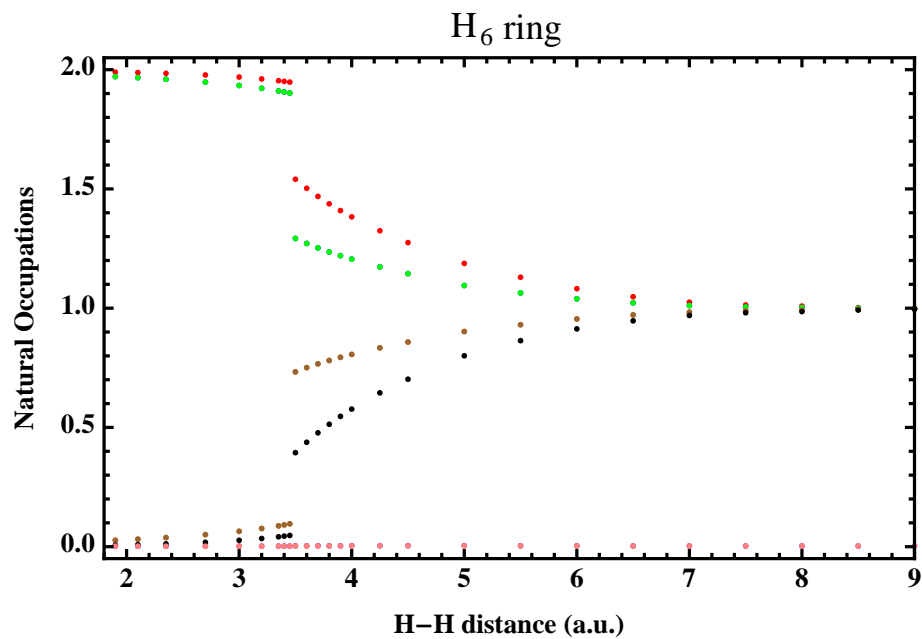


FIG. 3. Natural occupation numbers of the H₆ ring as calculated by GF2 with respect to H-H distance.

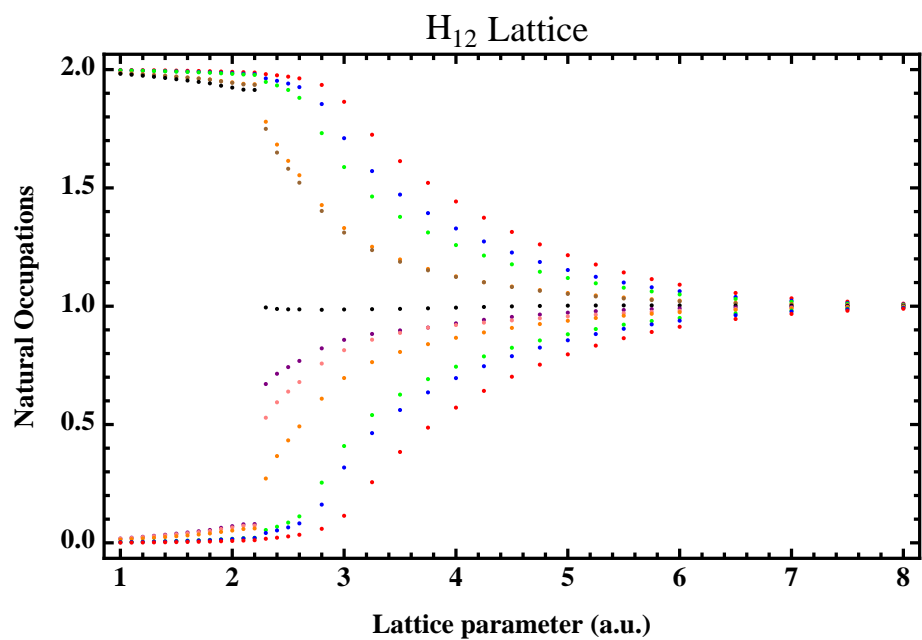


FIG. 4. Natural occupation numbers of the 4×3 H₁₂ lattice as calculated by GF2 with respect to lattice parameter.