

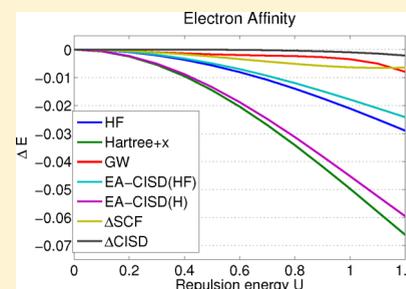
# Comparison between *GW* and Wave-Function-Based Approaches: Calculating the Ionization Potential and Electron Affinity for 1D Hubbard Chains

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**ABSTRACT:** We calculate the ionization potential and electron affinity of 1D Hubbard chains with a variety of different site energies from two perspectives: (i) the physics-based *GW* approximation and (ii) the chemistry-based configuration interaction (CI) approach. Results obtained from all methods are compared against the exact values for three classes of systems: metallic, impurity doped, and molecular (semiconducting/insulating) systems. Although all methods are reasonably accurate for weakly correlated systems, the *GW* method is significantly more reliable for strongly correlated systems with little disorder unless explicit double excitations are included in the CI. In principle, our results should offer some intuition about the choice of methodologies as well as state references for different classes of physical systems.



## I. INTRODUCTION

Calculations of the charged properties of materials have long been one of the major challenging goals in molecular systems and condensed matter physics. For a many-electron system, the Hamiltonian is given by

$$H = \sum_i \left[ -\frac{1}{2} \nabla^2(\mathbf{r}_i) + V(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

where  $V$  is a local external potential caused by nuclear-electronic coupling. Because of the last term in eq 1, which describes the Coulomb interaction between electrons, it is exponentially difficult to diagonalize an  $N$ -body Hamiltonian exactly. Of course, many approximate, mean-field theories have been developed within the single-particle approximation for the Coulomb term, which allow one to estimate the properties of large systems analytically. (A good review can be found in ref 1.) For instance, one can treat electrons as essentially noninteracting particles in theories such as the Hartree approximation or the Hartree–Fock (HF) approximation<sup>2</sup> so that the Hamiltonian becomes straightforward to solve.

When the Coulombic interactions are large and the picture of independent electrons breaks down,<sup>3</sup> electronic screening can no longer be neglected. On the one hand, quantum chemistry has traditionally sought either (i) improved exchange–correlation kernels within density-functional theory (DFT) or (ii) optimal wave function ansatzes.<sup>4–7</sup> For example, for several recent decades, quantum chemists were focused on local correlation techniques to calculate ground state properties.<sup>8–13</sup> On the other hand, condensed matter theorists usually treat correlated electrons (or holes) as approximately independent quasiparticles and correlation effects are addressed through many-body perturbation theory (MBPT) in terms of the self-energy of the

quasiparticles.<sup>14–16</sup> In the framework of Green’s functions,<sup>17,18</sup> the *GW* method is known to be the simplest working approximation for calculations of the self-energy.<sup>19–25</sup>

We believe that not yet enough work has been done by comparing the behavior of the *GW* method (which is popular in the physics community) and wave-function-based approaches (which are popular in the chemistry community) regarding the calculation of the ionization potential and electron affinity. This statement excludes recent works by (i) Bruneval et al., who compared *GW* against DFT and HF for atoms and molecules;<sup>26,27</sup> and (ii) McClain et al., who calculated the spectral function of the uniform electron gas via *ab initio* coupled-cluster theory and compared against *GW* results.<sup>28</sup> Notwithstanding refs 26–28, one difficulty in assessing different methodologies is the difficulty calculating exact benchmarks for ionization potentials and electron affinities.

With this background in mind, here we will calculate the electron affinities and ionization potentials for a set of 1D Hubbard chains<sup>29</sup> with either eight or ten sites and different possible site energies using exact diagonalization of the full Hamiltonian. Thereafter, approximate results can be evaluated for accuracy according to both the *GW* method and various wave-function-based quantum chemistry approaches. We analyze three different types of systems: metallic systems, doped systems, and molecular (semiconducting/insulating) systems. Although the original *GW* method is a computationally expensive self-consistent method, we will follow the so-called  $G_0W_0$  procedure proposed by Hybertsen and Louie in 1986<sup>30</sup> and perform a first-order perturbative calculation.

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An outline of this paper is as follows. In section II, we briefly review our model system and the methodologies applied in the calculation, both wave-function-based approaches and the *GW* method. In section III, we compare results given by the approximate methods versus the exact values for three different types of systems. In section IV, we discuss our results. In section V, we conclude.

Unless otherwise specified, we use lowercase latin letters to denote spin molecular orbitals (MO) ( $a, b, c, d$  for virtual orbitals,  $i, j, k, l, m$  for occupied orbitals,  $p, q, r, s, w$  for arbitrary orbitals) and Greek letters ( $\alpha, \beta, \gamma, \delta, \lambda, \sigma, \mu, \nu$ ) to denote atomic orbitals (AO). The electronic excited states obtained within the random-phase approximation (RPA) are denoted by  $\Psi$  (with uppercase indices I and J).

## II. THEORY

**II.A. Exact Diagonalization versus Orbital Energies.** For a system with  $N$  electrons, the exact ionization potential  $E_{\text{ion}}$  and affinity energy  $E_{\text{aff}}$  can be obtained from the total energy difference

$$E_{\text{ion}} = E_0^{N-1} - E_0^N \quad (2)$$

$$E_{\text{aff}} = E_0^N - E_0^{N+1} \quad (3)$$

Alternatively, the easiest scheme to estimate ionization energies ( $E_{\text{ion}}$ ) and electron affinities ( $E_{\text{aff}}$ ) is to evaluate the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy,<sup>31</sup> i.e.,

$$E_{\text{ion}} \approx -\epsilon_{\text{homo}} \quad (4)$$

$$E_{\text{aff}} \approx -\epsilon_{\text{lumo}} \quad (5)$$

Here, the orbital energies are taken from a HF calculation (or, of course, a DFT calculation). For a Hartree calculation, the ionization energies (electron affinities) are approximated by the HOMO (LUMO) energy plus the orbital exchange potential.

$$E \approx -\epsilon_p^{\text{H}} + \sum_i (p|ip) \quad p = \text{HOMO or LUMO} \quad (6)$$

where  $(pq|rs) = \int d\mathbf{r}d\mathbf{r}' \frac{\phi_p^*(\mathbf{r})\phi_q(\mathbf{r})\phi_r^*(\mathbf{r}')\phi_s(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$  refers to the Coulomb interaction. The zero of energy is a slow electron infinitely far away. As defined in eq 2–6, for a system that does not want to lose or accept another electron, the ionization potential is positive and the electron affinity is negative.

**II.B. IP/EA-CISD.** Beyond the Hartree/HF orbital energies, the simplest quantum chemistry approximation for  $E_{\text{ion}}$  is sometimes referred to as IP-CISD (Ionization Potential-Configuration Interaction with Singles and Doubles).<sup>32</sup> IP-CISD describes ionized states as 1h and 2h1p excitations from a closed-shell reference (usually HF) and the amplitudes of the target states are found by diagonalizing the bare Hamiltonian  $H$ . Here h denotes a hole and p denotes a particle. In some cases, IP-CISD can provide an accurate ionization potential for closed-shell systems.<sup>32</sup> Mathematically for IP-CISD, one constructs a variational wave function ansatz  $|\Psi\rangle = \sum_i t_i |\Phi_i\rangle + \sum_{ij} t_{ij}^a |\Phi_{ij}^a\rangle$ . By including one set of orbital excitations on top of the hole, one hopes to recover a reasonable amount of electronic correlation following ionization. To solve for a stationary state with coefficients  $t_i$  and  $t_{ij}^a$ , one diagonalizes a four-by-four-block Hamiltonian

$$H = \begin{pmatrix} H^{SS} & H^{SD} \\ H^{DS} & H^{DD} \end{pmatrix} \quad (7)$$

where  $H_{i,k}^{SS} = \langle \Phi_i | H | \Phi_k \rangle$ ,  $H_{i,kl}^{SD} = \langle \Phi_i | H | \Phi_{kl}^b \rangle$ ,  $H_{ij,k}^{DS} = \langle \Phi_{ij}^a | H | \Phi_k \rangle$ , and  $H_{ab,kl}^{DD} = \langle \Phi_{ab}^a | H | \Phi_{kl}^b \rangle$ . The same logic above can be applied when the electron affinity ( $E_{\text{aff}}$ ) is computed, which is the amount of energy released when an electron is added to an unoccupied orbital. The simplest Hamiltonian for evaluating the electron affinity (titled EA-CISD) contains the following matrix elements:  $H^{SS} = \langle \Phi^a | H | \Phi^c \rangle$ ,  $H_{ij}^{SD} = \langle \Phi^a | H | \Phi_{ij}^{cd} \rangle$ ,  $H_{abi,c}^{DS} = \langle \Phi_i^{ab} | H | \Phi^c \rangle$ , and  $H_{abi,jdc}^{DD} = \langle \Phi_i^{ab} | H | \Phi_{jdc}^{cd} \rangle$ .

It should be emphasized that neither IP-CISD nor EA-CISD is very computationally cheap. These methods require the diagonalization of a matrix of size  $N_{\text{occ}}^2(N_{\text{virt}} + 1)^2$  or  $N_{\text{virt}}^2(N_{\text{occ}} + 1)^2$ . Nevertheless, they are the most inexpensive, straightforward wave function approaches.

Finally, we mention that, in principle, one can compute IP/EA-CISD energies using either a Hartree or HF reference. Below we will perform such calculations with both references for the Hubbard model and, after extracting the electron affinities and ionization potentials, we will compare results.

**II.C.  $\Delta$ SCF and  $\Delta$ CISD.** Another way to evaluate the ionization potential and electron affinity is to compute  $E_0^{N-1}$ ,  $E_0^N$ , and  $E_0^{N+1}$  directly, and here we will calculate such quantities in two ways: (i) a simple self-consistent field (SCF) calculation, denoted  $\Delta$ SCF; (ii) and a more sophisticated configuration interaction singles and doubles (CISD) calculation, denoted  $\Delta$ CISD.

Mathematically for CISD, one constructs a wave function according to the ansatz

$$|\Psi\rangle = t_{\text{HF}} |\Psi_{\text{HF}}\rangle + \sum_{ai} t_i^a |\Phi_i^a\rangle + \sum_{ijab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (8)$$

where  $|\Psi_{\text{HF}}\rangle$  is the HF ground state with the coefficient  $t_{\text{HF}}$ , and  $|\Phi_i^a\rangle$  and  $|\Phi_{ij}^{ab}\rangle$  are single and double excitations with coefficients  $t_i^a$  and  $t_{ij}^{ab}$ , respectively. One diagonalizes a CISD Hamiltonian of the form

$$H = \begin{pmatrix} E_{\text{HF}} & 0 & H^{\text{OD}} \\ 0 & H^{SS} & H^{\text{SD}} \\ (H^{\text{OD}})^\dagger & (H^{\text{SD}})^\dagger & H^{\text{DD}} \end{pmatrix} \quad (9)$$

where  $E_{\text{HF}}$  is the HF ground state energy,  $H_{ijab}^{\text{OD}} = \langle \Psi_{\text{HF}} | H | \Phi_{ij}^{ab} \rangle$ ,  $H_{ia,jb}^{SS} = \langle \Phi_i^a | H | \Phi_{jb}^b \rangle$ ,  $H_{ia,jbkc}^{\text{SD}} = \langle \Phi_i^a | H | \Phi_{jbc}^b \rangle$ , and  $H_{ijab,kcld}^{\text{DD}} = \langle \Phi_{ij}^{ab} | H | \Phi_{kl}^{cd} \rangle$ . Note that the manifold of single excitations does not couple to the ground state according to Brillouin's theorem.

**II.D. *GW* Method.** *II.D.1. Green's Function Review.* The one-body time-ordered Green's function  $G^t$  can be written as

$$G^t(\mathbf{r}, t; \mathbf{r}', t') \equiv \langle \Psi_0^N | \hat{T} [\hat{a}(\mathbf{r}, t) \hat{a}^\dagger(\mathbf{r}', t')] | \Psi_0^N \rangle \quad (10)$$

where  $|\Psi_0^N\rangle$  is the ground state for an interacting  $N$ -body system,  $\hat{a}(\mathbf{r}, t)$  is the electron annihilation operator which annihilates an electron at  $(\mathbf{r}, t)$ , and  $\hat{T}$  is the Fermionic time-ordering operator. Equation 10 is the starting point for MBPT.

For our purposes (to get the ionization potentials and electron affinities), *GW* calculations require only the noninteracting Green's function where  $|\Psi_0^N\rangle$  is a Slater determinant. In the frequency domain, one can then write down the expression for the noninteracting time-ordered Green's function as (in the MO basis)

$$G^t(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{\phi_i(\mathbf{r}) \phi_i(\mathbf{r}')}{\omega - \varepsilon_i - i\eta} + \sum_a \frac{\phi_a(\mathbf{r}) \phi_a(\mathbf{r}')}{\omega - \varepsilon_a + i\eta} \quad (11)$$

$$\equiv G_{\text{occ}}^R(\mathbf{r}, \mathbf{r}', \omega) - G_{\text{virt}}^A(\mathbf{r}, \mathbf{r}', \omega) \quad (12)$$

Equation 11 defines the “ $G$ ” in the GW method. In eq 12, we have defined  $G_{\text{occ}}^R$  and  $G_{\text{virt}}^A$  as per the usual convention that electrons move forward in time and holes move backward in time. Thus, it is straightforward to show that  $i\hbar G_{\text{occ}}^R(\mathbf{r}, \mathbf{r}', t-t')$  ( $i\hbar G_{\text{virt}}^A(\mathbf{r}, \mathbf{r}', t-t')$ ) is the probability amplitude for the propagation of an additional electron (hole) from  $(\mathbf{r}', t')$  to  $(\mathbf{r}, t)$  for a noninteracting system.

**II.D.2. Screened Coulomb Interaction.** To express the “ $W$ ” in the GW approximation, we need a few definitions. Classically, if an external potential  $u(\mathbf{r}, t)$  is applied to a solid, the screening of the solid is defined in terms of a dielectric constant. In many-body theory, the inverse of the dielectric response is defined as

$$\varepsilon^{-1}(\mathbf{r}, t; \mathbf{r}', t') \equiv \left. \frac{\delta V(\mathbf{r}, t)}{\delta u(\mathbf{r}', t')} \right|_{u=0} \quad (13)$$

where  $V(\mathbf{r}, t)$  is the combination of the external potential and the Coulomb potential created by the induced charge (with density  $\rho$ )

$$V(\mathbf{r}, t) \equiv u(\mathbf{r}, t) + \int d\mathbf{r}' v(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', t) \quad (14)$$

The inverse of the dielectric response can be rewritten as

$$\varepsilon^{-1}(\mathbf{r}, t; \mathbf{r}', t') = \delta_{\mathbf{r}\mathbf{r}'} \delta_{tt'} + \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \frac{\delta \rho(\mathbf{r}'', t'')}{\delta u(\mathbf{r}', t')} \Big|_{u=0} \quad (15)$$

In linear response theory, the response function (or the so-called RPA polarizability)  $\chi$  is defined to describe the change of the induced charge density if the external potential undergoes a small change

$$\chi(\mathbf{r}, t; \mathbf{r}', t') \equiv \left. \frac{\delta \rho(\mathbf{r}, t)}{\delta u(\mathbf{r}', t')} \right|_{u=0} \quad (16)$$

Using the chain rule for functional derivatives, we can express  $\chi$  in terms of the noninteracting response function as

$$\chi(\mathbf{r}, t; \mathbf{r}', t') = \int d\mathbf{r}'' dt'' \frac{\delta \rho(\mathbf{r}, t)}{\delta V(\mathbf{r}'', t'')} \frac{\delta V(\mathbf{r}'', t'')}{\delta u(\mathbf{r}', t')} \Big|_{u=0} \quad (17)$$

$$\equiv \int d\mathbf{r}'' dt'' P(\mathbf{r}, t; \mathbf{r}'', t'') \varepsilon^{-1}(\mathbf{r}'', t''; \mathbf{r}', t') \quad (18)$$

where we define the noninteracting response function as

$$P(\mathbf{r}, t; \mathbf{r}', t') \equiv \left. \frac{\delta \rho(\mathbf{r}, t)}{\delta V(\mathbf{r}', t')} \right|_{u=0} \quad (19)$$

In the GW approximation,  $P(\mathbf{r}, \mathbf{r}', t-t')$  can be expressed as the multiplication of two Green’s functions (by neglecting the vertex function)

$$P(\mathbf{r}, t; \mathbf{r}', t') = -i\hbar G^t(\mathbf{r}, t; \mathbf{r}', t') G^t(\mathbf{r}', t'; \mathbf{r}, t) \quad (20)$$

If we apply the definition of the RPA polarizability (eq 16), the inverse of the dielectric response (eq 15) becomes

$$\varepsilon^{-1}(\mathbf{r}, t; \mathbf{r}', t') = \delta_{\mathbf{r}\mathbf{r}'} \delta_{tt'} + \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', t''; \mathbf{r}', t') \quad (21)$$

In the frequency domain, the screened Coulomb interaction is defined as

$$W(\mathbf{r}, \mathbf{r}'; \omega) \equiv \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega) v(\mathbf{r}'', \mathbf{r}') \quad (22)$$

Taking the Fourier transform of eq 21 and plugging the result into eq 22, we find  $W(\mathbf{r}, \mathbf{r}'; \omega)$  can be rewritten as

$$W(\mathbf{r}, \mathbf{r}'; \omega) = v(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' d\mathbf{r}''' v(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}'''; \omega) v(\mathbf{r}''', \mathbf{r}') \quad (23)$$

The screened Coulomb interaction  $W(\mathbf{r}, \mathbf{r}'; \omega)$  is the effective potential at  $\mathbf{r}'$  induced by a quasiparticle at  $\mathbf{r}$ ; in general,  $W(\mathbf{r}, \mathbf{r}'; \omega)$  is anticipated to be weaker and better behaved than the bare Coulomb interaction  $v(\mathbf{r}, \mathbf{r}')$ . The difference between  $W(\mathbf{r}, \mathbf{r}'; \omega)$  and  $v(\mathbf{r}, \mathbf{r}')$  is the polarizable part of the screened Coulomb interaction  $W_p$

$$W_p(\mathbf{r}, \mathbf{r}'; \omega) \equiv W(\mathbf{r}, \mathbf{r}'; \omega) - v(\mathbf{r}, \mathbf{r}') \quad (24)$$

$$= \int d\mathbf{r}'' d\mathbf{r}''' v(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}'''; \omega) v(\mathbf{r}''', \mathbf{r}') \quad (25)$$

$W_p$  is the “ $W$ ” in the GW approximation that must now be evaluated.

**II.D.3. RPA Polarizability.** To calculate the RPA polarizability  $\chi$ , the usual prescription is to perform a RPA calculation on top of a Hartree reference state, ignoring all exchange terms. The RPA working equation is given by<sup>33</sup>

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} = \Omega_I \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} \quad (26)$$

for excitation amplitudes  $\mathbf{X}^I$  and  $\mathbf{Y}^I$  and excitation energy  $\Omega_I$  for RPA excited state  $I$ .  $\mathbf{A}$  and  $\mathbf{B}$  contain matrix elements as follows

$$A_{iajb} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) - (ialjb) \quad (27)$$

$$B_{iajb} = -(ialbj) \quad (28)$$

By diagonalizing the RPA non-Hermitian Hamiltonian, one obtains the excitation amplitudes  $\mathbf{X}^I$  and  $\mathbf{Y}^I$  and the excitation energy  $\Omega_I$  for each RPA excited state  $I$ . The RPA polarizability can then be computed via the following sum-overstates expression<sup>34</sup>

$$\begin{aligned} \chi(\omega) &= \left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix} \right]^{-1} \\ &= \sum_I \left[ \frac{1}{\Omega_I + \omega} \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} (\mathbf{X}^I \ \mathbf{Y}^I) + \frac{1}{\Omega_I - \omega} \begin{pmatrix} \mathbf{Y}^I \\ \mathbf{X}^I \end{pmatrix} (\mathbf{Y}^I \ \mathbf{X}^I) \right] \end{aligned} \quad (29)$$

In terms of MOs, if the perturbing potential is of the form  $u_{jb}(t)(a_b^\dagger a_j + a_j^\dagger a_b)$ , one finds that the response function is

$$\chi_{iajb}(\omega) = \sum_I \left[ \frac{M_{iajb}^I}{\Omega_I + \omega} + \frac{M_{iajb}^I}{\Omega_I - \omega} \right] \quad (30)$$

where

$$M_{iajb}^I = X_{ia}^I X_{jb}^I + X_{ia}^I Y_{jb}^I + Y_{ia}^I X_{jb}^I + Y_{ia}^I Y_{jb}^I \quad (31)$$

To express  $\chi$  in a real space, one must sum over orbitals

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) &= \sum_I \sum_{iajb} \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \phi_j(\mathbf{r}') \phi_b(\mathbf{r}') \left[ \frac{M_{iajb}^I}{\Omega_I + \omega} + \frac{M_{iajb}^I}{\Omega_I - \omega} \right] \end{aligned} \quad (32)$$

**II.D.4. Self-Energy.** In practice, the *GW* self-energy is obtained from the frequency convolution of Green's function  $G^t$  with the screened Coulomb interaction  $W$

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' e^{i\eta\omega'} G^t(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}', \mathbf{r}, \omega') \quad (33)$$

where  $\eta$  is an infinitesimal positive real number. Introducing  $W_p$  (eq 25) can split the self-energy into two parts: the static exchange part  $\Sigma^x$  and the dynamic correlation part  $\Sigma^c$

$$\Sigma^x(\mathbf{r}, \mathbf{r}') = \frac{i}{2\pi} \nu(\mathbf{r}, \mathbf{r}') \int d\omega' e^{i\eta\omega'} G^t(\mathbf{r}, \mathbf{r}', \omega') \quad (34)$$

$$\Sigma^c(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' e^{i\eta\omega'} G^t(\mathbf{r}, \mathbf{r}', \omega + \omega') W_p(\mathbf{r}', \mathbf{r}, \omega') \quad (35)$$

Note that  $\Sigma^x$  corresponds to the usual nonlocal exchange potential, which is introduced by the Fock exchange operator in the HF approximation

$$\Sigma_{pq}^x = - \sum_i \sum_{\mu\nu\lambda\sigma} (\mu\nu|\lambda\sigma) C_{\mu p} C_{\nu i} C_{\lambda i} C_{\sigma q} \quad (36)$$

In eq 36 and everywhere below, we assume we are performing a *GW* calculation on top of a Hartree calculation. All orbitals are Hartree orbitals.

$\Sigma^c$  gives rise to the correlation energy of the system, which is not taken into consideration in a HF calculation. To evaluate the  $\Sigma^c$  contribution to the self-energy from the *GW* method, one simply plugs eqs 11 and 32 into eq 37 and obtains the final expression for correlation part of the self-energy (in the MO basis). Plugging eq 25 into eq 35, one can express  $\Sigma^c$  in terms of Green's function  $G^t$ , the RPA polarizability  $\chi$ , and the bare Coulomb potential  $\nu$

$$\begin{aligned} \Sigma^c(\mathbf{r}, \mathbf{r}', \omega) &= \frac{i}{2\pi} \int d\omega' e^{i\eta\omega'} G^t(\mathbf{r}, \mathbf{r}', \omega + \omega') \\ &\times \int d\mathbf{r}'' d\mathbf{r}''' \nu(\mathbf{r}', \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}''', \omega') \nu(\mathbf{r}''', \mathbf{r}) \end{aligned} \quad (37)$$

The self-energy evaluated at the energy of Hartree orbital  $s$  can finally be expressed as

$$\begin{aligned} \Sigma_{pq}^c(\varepsilon_s^H) &= \sum_{j b k c} \sum_I \left( \sum_i \frac{(i p | j b)(i q | k c)}{\varepsilon_s^H - \Omega_I - \varepsilon_i^H - i\eta} \right. \\ &\left. + \sum_a \frac{(a p | j b)(a q | k c)}{\varepsilon_s^H + \Omega_I - \varepsilon_a^H + i\eta} \right) M_{j b k c}^I \end{aligned} \quad (38)$$

For self-consistency, we must have

$$\varepsilon_s^{GW} = \varepsilon_s^H + \Sigma_{ss}(\varepsilon_s^{GW}) \quad (39)$$

If we want to avoid a self-consistent calculation, the standard approach is to apply the linear expansion for the real part of the  $\Sigma^c(\omega)$

$$\text{Re } \Sigma^c(\varepsilon_s^{GW}) \approx \text{Re } \Sigma^c(\varepsilon_s^H) + \frac{\varepsilon_s^{GW} - \varepsilon_s^H}{\hbar} \frac{\partial \text{Re } \Sigma^c(\varepsilon_s^H)}{\partial \omega} \quad (40)$$

which leads to

$$\varepsilon_s^{GW} \approx \varepsilon_s^H + Z_s \text{Re } \Sigma^c(\varepsilon_s^H) + \Sigma_s^x \quad (41)$$

The quasiparticle renormalization factor “ $Z_s$ ” is given by

$$Z_s \equiv \left( 1 - \frac{\partial \text{Re } \Sigma^c(\varepsilon_s^H)}{\partial \omega} \right)^{-1} \quad (42)$$

According to eqs 4 and 5, the electron affinity/ionization potential of a system can be obtained from the *GW* approximation by taking the negative value of eq 41. At this point, all of the formal theory has been presented and will be applied to a 1D Hubbard model system.

### II.E. Model System and Its Affinity/Ionization Potential.

The Hubbard model offers one of the simplest ways to get insight into how the interactions between electrons can give rise to insulating, doped, and conducting effects in a solid. In this work we take 1D Hubbard model as our testing system, which is described by the Hamiltonian

$$\begin{aligned} \mathcal{H} &\equiv \tau \sum_{\langle \mu \nu \rangle} (a_\mu^\dagger a_\nu + \bar{a}_\mu^\dagger \bar{a}_\nu) + V_\mu \sum_\mu (a_\mu^\dagger a_\mu + \bar{a}_\mu^\dagger \bar{a}_\mu) \\ &+ \sum_\mu U_\mu a_\mu^\dagger \bar{a}_\mu^\dagger a_\mu \bar{a}_\mu \end{aligned} \quad (43)$$

where  $\mu$  denotes the site of the system,  $\tau$  is the hopping integral between neighboring sites,  $V_\mu$  is the on-site energy (for site  $\mu$ ), and  $U_\mu$  is the repulsion energy between two electrons of opposite spin accommodated on each site  $\mu$ . A bar indicates spin down.

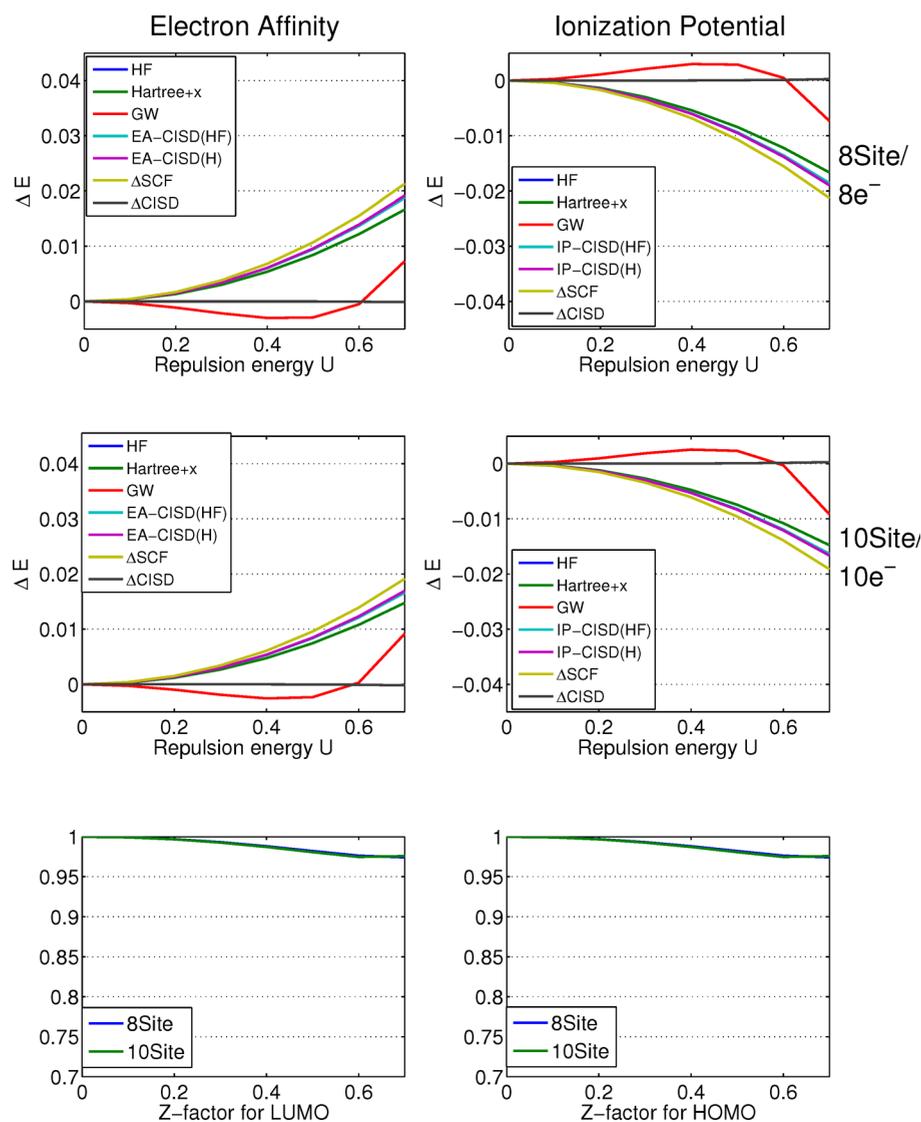
In practice, we first perform a normal Hartree calculation for the model system, obtaining the Hartree orbital energy  $\varepsilon_i^H$  and the molecular orbital coefficients  $C$ . The next step is to perform a time-dependent Hartree calculation within RPA to get the matrix elements for the RPA polarizability  $\chi$ . Then eq 38 becomes (for the HOMO and LUMO respectively)

$$\begin{aligned} \Sigma^c(\varepsilon_{\text{homo}}^H) &= \sum_{j b k c} \sum_I \left( \sum_i \frac{C_{\mu i} C_{\nu i}}{\varepsilon_{\text{homo}}^H - \Omega_I - \varepsilon_i^H - i\eta} \right. \\ &+ \left. \sum_a \frac{C_{\mu a} C_{\nu a}}{\varepsilon_{\text{homo}}^H + \Omega_I - \varepsilon_a^H + i\eta} \right) \\ &\times U_\mu U_\nu C_{\mu p} C_{\mu j} C_{\mu b} C_{\nu q} C_{\nu k} C_{\nu c} M_{j b k c}^I \end{aligned} \quad (44)$$

$$\begin{aligned} \Sigma^c(\varepsilon_{\text{lumo}}^H) &= \sum_{j b k c} \sum_I \left( \sum_i \frac{C_{\mu i} C_{\nu i}}{\varepsilon_{\text{lumo}}^H - \Omega_I - \varepsilon_i^H - i\eta} \right. \\ &+ \left. \sum_a \frac{C_{\mu a} C_{\nu a}}{\varepsilon_{\text{lumo}}^H + \Omega_I - \varepsilon_a^H + i\eta} \right) \\ &\times U_\mu U_\nu C_{\mu p} C_{\mu j} C_{\mu b} C_{\nu q} C_{\nu k} C_{\nu c} M_{j b k c}^I \end{aligned} \quad (45)$$

The exchange part of the self-energy  $\Sigma^x$  for the 1D Hubbard model is given by

$$\Sigma_{pq}^x = \sum_i \sum_\mu U_\mu C_{\mu p} C_{\mu q} C_{\mu i}^2 \quad (46)$$



**Figure 1.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor (eq 42) for the metallic system ( $V_\mu = 0$  for all sites  $\mu$ ,  $\tau = 1.0$ ). All errors are relative to the exact diagonalization. The upper and middle panels show the results for 8-Site/ $8e^-$  and 10-Site/ $10e^-$ , respectively; the left and right of the top two panels show the electron affinity and ionization energy differences respectively; and the lower panel shows the  $Z$  factor for LUMO and HOMO. Note that  $\Delta$ CISD performs the best for metallic systems followed by the GW method.

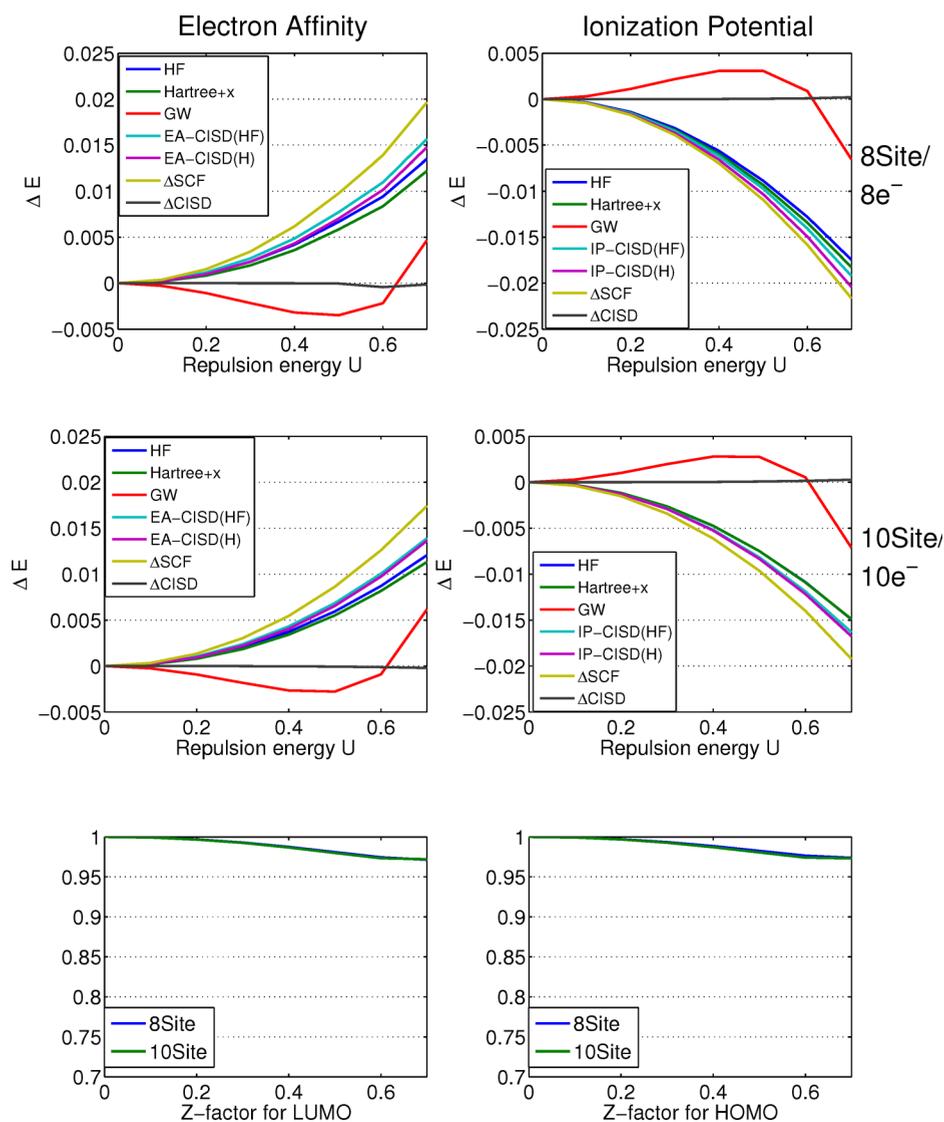
Note that for all calculations below, we calculate only HOMO and LUMO energies and we set  $\eta = 0$  in eqs 44 and 45.

### III. RESULTS

We apply the theory above to 1D Hubbard models of two sizes: 8-Site and 10-Site. We assume half-filling with either 8 or 10 electrons, respectively. The hopping integral between neighboring sites  $\tau$  is set to be 1.0 for all systems, while the electron repulsion energy  $U$  is varied. All quantities will be calculated in a.u. henceforward. Exact electron affinities and ionization potentials are obtained by diagonalizing the Hamiltonian with Davidson iterative diagonalization.<sup>35</sup> To compare the behaviors of different methods for different cases, we will plot the difference between the computed value and the exact answer as follows: the upper and middle panels show the results for 8-Site/ $8e^-$  and 10-Site/ $10e^-$ , respectively; the left and right of the top two panels show the electron affinity and ionization energy differences respectively; the lower panel shows the  $Z$  factor for LUMO and HOMO (eq 42).

**III.A. Metallic System.** We first study metallic systems. In metallic systems, every site has the same on-site energy ( $V_\mu = 0$  for all sites  $\mu$ ).<sup>36</sup> The electron repulsion energy  $U$  is varied from 0 to 0.7. Results are shown in Figure 1. Focusing on the electron affinity (left panel), one can see that all approximate methods give the exact answer when  $U = 0$  (of course). As  $U$  increases, the errors given by all the quantum chemistry methods (except  $\Delta$ CISD) increase dramatically, indicating the failure of these methods for strongly correlated systems. By contrast, the GW method, with a maximum error ( $\sim 0.01$ ) when  $U = 0.7$ , performs fairly well (though not as well as  $\Delta$ CISD, which gives almost exact results). The validation of the GW approximation for the metallic system is also strengthened by the fact that the  $Z$  factor for both 8-Site and 10-Site is very close to 1. Similar results are found for the ionization potential.

Note that, if we want to plot the total HOMO/LUMO gap ( $\epsilon_{\text{lumo}} - \epsilon_{\text{homo}}$  or equivalently,  $E_{\text{ion}} - E_{\text{aff}}$ ) for such systems, the quantum chemistry methods (except  $\Delta$ CISD) would still perform very poorly; the errors for  $E_{\text{ion}}$  and  $E_{\text{aff}}$  have different signs and subtracting these errors would yield even larger errors.



**Figure 2.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor for the metallic system for the doped system (with  $V_5 = -0.5$  for the 8-Site system and  $V_6 = -0.5$  for the 10-Site system; for all other sites,  $V_\mu = 0$ ).  $\tau = 1.0$ . All errors are relative to the exact diagonalization.  $\Delta$ CISD is still the most accurate method and GW consistently outperforms other wave function methods.

**III.B. Doped Impurity Systems.** By lowering the energy of a single site in the metallic system, one can model an impurity, which dopes an otherwise metallic system and can influence the overall photoactivity or electrical properties of the total system. In Figures 2 and 3, we calculate results for electron repulsion energies  $U$  between 0 and 0.7. We consider two on-site energies:  $V_{\text{imp}} = -0.5$  (Figure 2) and  $V_{\text{imp}} = -1.0$  (Figure 3).

For the case  $V_{\text{imp}} = -0.5$  (where the impurity energy is half as large as the hopping integral  $\tau$ ), it can be seen in Figure 2 that the results are roughly identical to those for the metallic case:  $\Delta$ CISD gives the most accurate results and the GW method is better compared with other quantum chemistry methods.

For the case  $V_{\text{imp}} = -1.0$  (where the on-site energy is comparable with the hopping integral), the same conclusion holds only for the ionization energies. For the affinity energies (left panel of Figure 3), the quantum chemistry approaches now do much better than before (and  $\Delta$ CISD is again the best). In particular, the Hartree approximation with the exchange energy competes with GW for the most accurate method except  $\Delta$ CISD. The ionization energy results remain very similar to those of the

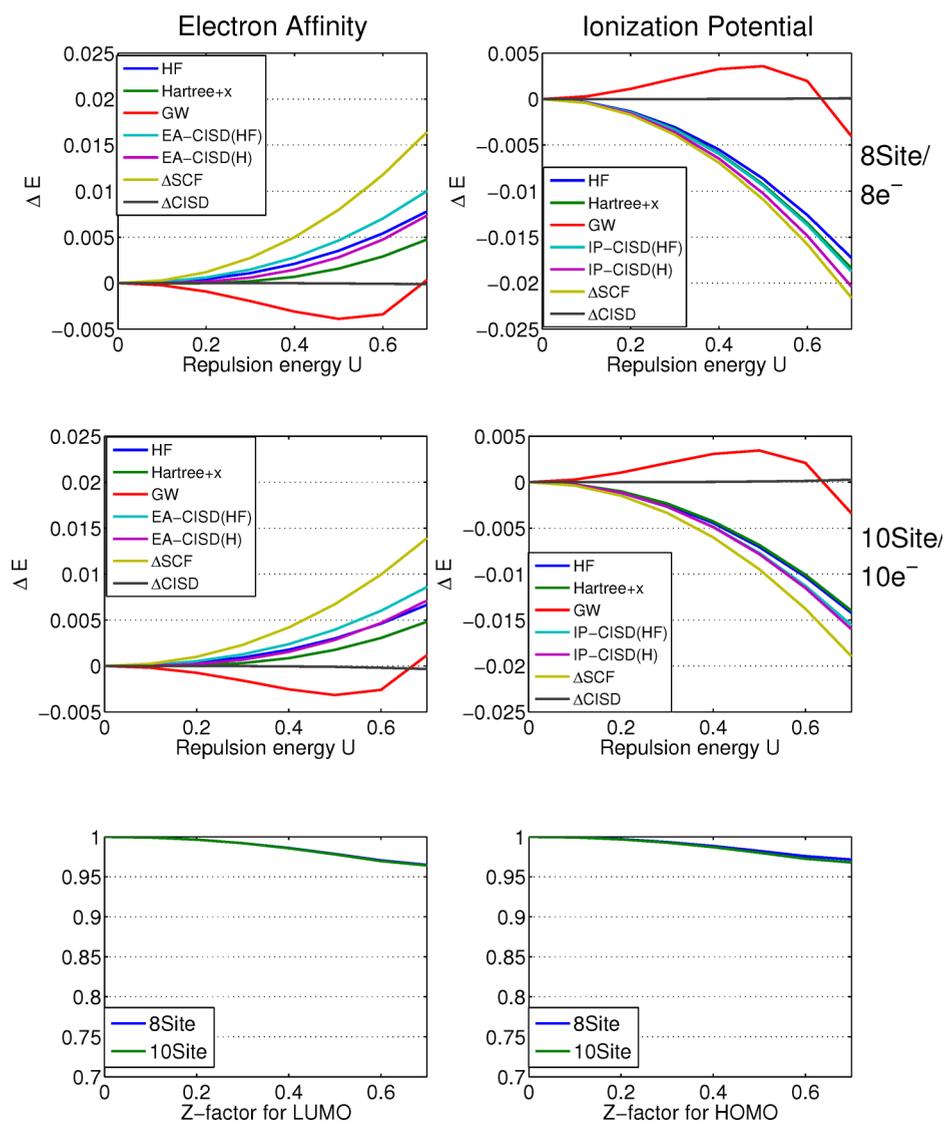
former cases; that is,  $\Delta$ CISD gives almost exact results and GW performs much better than other quantum chemistry methods.

In all doped systems, we note that the IP/EA-CISD methods yield results that are even worse than direct Hartree/HF approximations.

### III.C. Molecular (Semiconducting/Insulating) Systems.

To simulate a “molecular” Hubbard model, we construct an alternating Hamiltonian, whereby  $V_{\text{even}}$  is significantly lowered relative to  $V_{\text{odd}} = 0$ . In doing so, we expect that orbitals with lower energies will be doubly occupied and well separated from virtual orbitals. Thus, by creating an energy gap, we should be simulating closed-shell insulators and/or semiconductors (depending on the gap size).

For “molecular” systems with a small energy gap ( $V_{\text{even}} = -0.5$ ), the electron repulsion energy  $U$  is varied from 0 to 0.8. As shown in Figure 4, the performances of the quantum chemistry methods are now far improved compared with the metallic case. Although  $\Delta$ CISD remains the best, the Hartree and HF approximations compete with the GW method for accuracy and sometimes they prevail. As in Figures 2 and 3, the GW error



**Figure 3.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor for the doped system (with  $V_5 = -1.0$  for the 8-Site system and  $V_6 = -1.0$  for the 10-Site system; for all other sites,  $V_\mu = 0$ ).  $\tau = 1.0$ . All errors are relative to the exact diagonalization. Clearly,  $\Delta$ CISD again gives the most accurate results.  $GW$  performs better for ionization potentials than other quantum chemistry approach, but the Hartree approximation with exchange energy performs equally well for the electron affinity.

turns over as  $U$  gets larger; the  $GW$  error is maximized at some intermediate value of  $U$ .

It should be pointed out that, so far, the IP/EA-CISD methods have not provided any results better than the direct HF or Hartree approximation. In fact, wave function corrections to Hartree/HF calculations only increased the error in Figure 4. However, one must be careful not to quickly extrapolate from the data above. For “molecular” systems with an energy gap equal to the hopping integral ( $V_{\text{even}} = -1.0$ ), Figure 5 demonstrates that our results are completely different from the previous case ( $V_{\text{even}} = -0.5$ ). In particular, now, IP/EA-CISD methods are consistently more accurate than the direct HF or Hartree approximation. For the 8-Site system, IP/EA-CISD(HF) yields the overall best results apart from  $\Delta$ CISD. For the 10-Site system,  $\Delta$ CISD is followed by  $\Delta$ SCF and  $GW$ , which are better than the other approaches.

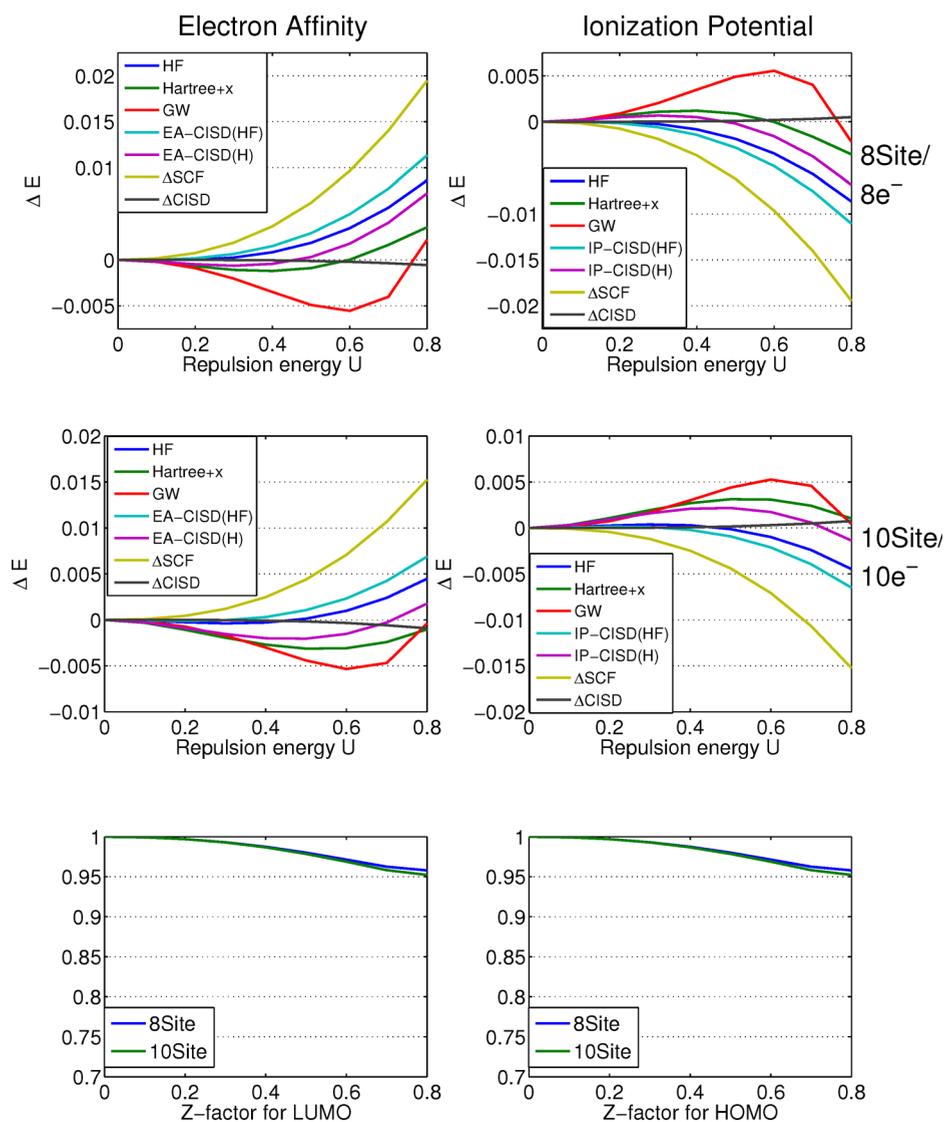
Lastly, unlike previous cases, according to Figure 5, the Hartree approximation yields remarkably large errors. As one would expect, the quality of the Hartree reference simply

degrades as the system becomes more molecular (and exact exchange becomes critical).

Finally, we consider the final, extreme “molecular” case whereby the on-site energy difference is now twice as large as the hopping integral ( $V_{\text{even}} = -2.0$ ). As Figure 6 shows, as  $U$  increases from 0 to 1.2,  $GW$  and  $\Delta$ SCF are quite accurate, though slightly worse than  $\Delta$ CISD. By contrast, the HF related methods perform worse than  $GW$ , and the Hartree related methods are even worse: the Hartree orbital energies are no longer any good.

#### IV. DISCUSSION

The results above (in section III) have compared the more chemical (wave function) versus the more physical ( $GW$ ) methods for calculating electron affinities and ionization energies. Of all the methods considered excluding  $\Delta$ CISD,  $GW$  is usually the most reliable approach when we consider a broad range of systems. This preliminary conclusion might be a bit surprising from the quantum chemistry point of view. After all, on the one hand, with regards to scaling,  $GW$  is limited by



**Figure 4.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor for “molecular” Hubbard models ( $V_{\text{even}} = -0.5$ ,  $V_{\text{odd}} = 0$ ,  $\tau = 1.0$ ). All errors are relative to the exact diagonalization. Here, though  $\Delta\text{CISD}$  is always the most accurate, the simple Hartree approximation with the exchange energy performs better than other methods. The  $\text{GW}$  approximation is still reasonable, which can also be shown from the  $Z$  factor values.

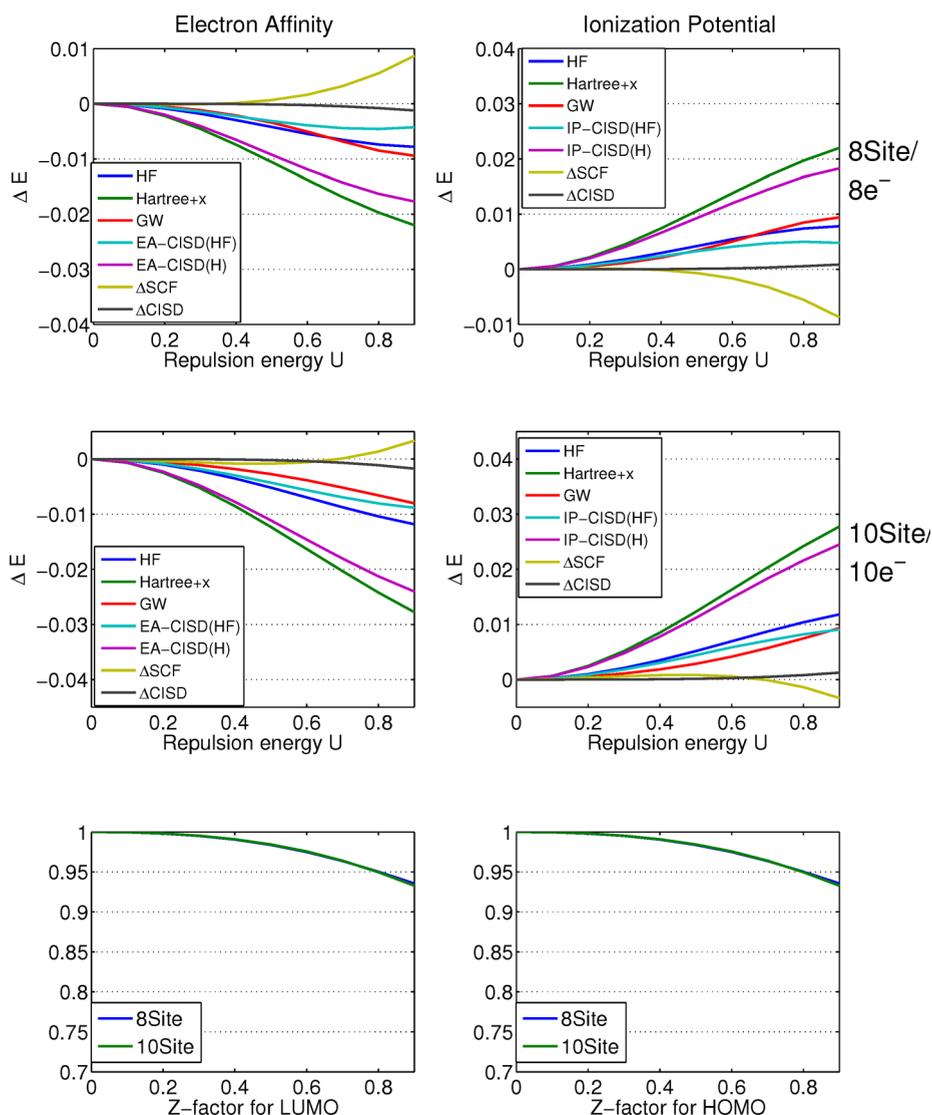
diagonalizing a matrix of order  $N_{\text{occ}}N_{\text{virt}} \times N_{\text{occ}}N_{\text{virt}}$ . On the other hand, the IP/EA-CISD methods require the diagonalization of comparatively larger matrices of order  $N_{\text{occ}}N_{\text{virt}}^2 \times N_{\text{occ}}N_{\text{virt}}^2$  (for EA-CISD). Thus,  $\text{GW}$  is able to provide improved results with less computational effort.

To understand this strong performance by  $\text{GW}$ , we investigate a simplified version of IP/EA-CISD, that is, fixing a single MO (HOMO for the ionization potential and LUMO for the electron affinity) and making corrections on top of this single orbital. Taking the 8-Site/ $8e^-$  “molecular” system ( $V_{\text{even}} = -1.0$ ) as an example, we compare the result of this so-called IP-CISD(HF/homo) or EA-CISD(HF/lumo) result against HF, IP/EA-CISD(HF), and  $\text{GW}$  results in Figure 7. For the electron affinity, EA-CISD(HF/lumo) provides a result very similar to that by direct HF but with some small improvement. For the ionization energy, IP-CISD(HF/homo) yields a noticeable correction and the result is much closer to the full IP-CISD(HF) energy. In other words, a single-orbital approximation for the hole does not degrade the answers significantly. Thus, there are clearly Hamiltonians for which quantum chemistry wave function

approaches can outperform  $\text{GW}$  with the same computational cost. (IP-CISD(homo) and EA-CISD(lumo) require the same computational cost as  $\text{GW}$ .)

That being said, in general,  $\text{GW}$  does outperform a more expensive algorithm. Obviously, the strength of  $\text{GW}$  is that the  $\text{GW}$  self-energy includes a summation of Coulomb interactions by diagonalizing the RPA matrix and constructing the full response matrix (which leads to the screening potential  $W$ ). By contrast, the IP/EA-CISD methods include only one bare Coulomb interaction through variational calculations. Thus, the results above reflect the relative value of these two approaches, and the  $\text{GW}$  approach would appear to be more robust overall.

Given that the  $\text{GW}$  performs so well above for a range of model Hubbard Hamiltonians, it is worthwhile to test its convergence with respect to the number of RPA states included. Considering eq 37, we see that the  $\text{GW}$  self-energy directly depends on the RPA polarizability  $\chi$ , the polarizability can be written as a sum over states (eq 32), and all excited states contributions to the self-energy will decay inversely proportional to the energy of that excited state. It is well-known that  $\text{GW}$  converges poorly with the



**Figure 5.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor for “molecular” Hubbard models ( $V_{\text{even}} = -1.0$ ,  $V_{\text{odd}} = 0$ ,  $\tau = 1.0$ ). All errors are relative to the exact diagonalization. Although  $\Delta\text{CISD}$  remains the most accurate, the Hartree approximation now performs the worst. Excluding  $\Delta\text{CISD}$ , IP/EA-CISD(HF) yields the overall best results for the 8-Site system whereas  $\Delta\text{SCF}$  and GW become the best for the 10-Site system,.

number of virtual orbitals,<sup>37,38</sup> but we would like to test this convergence for different Hamiltonians.

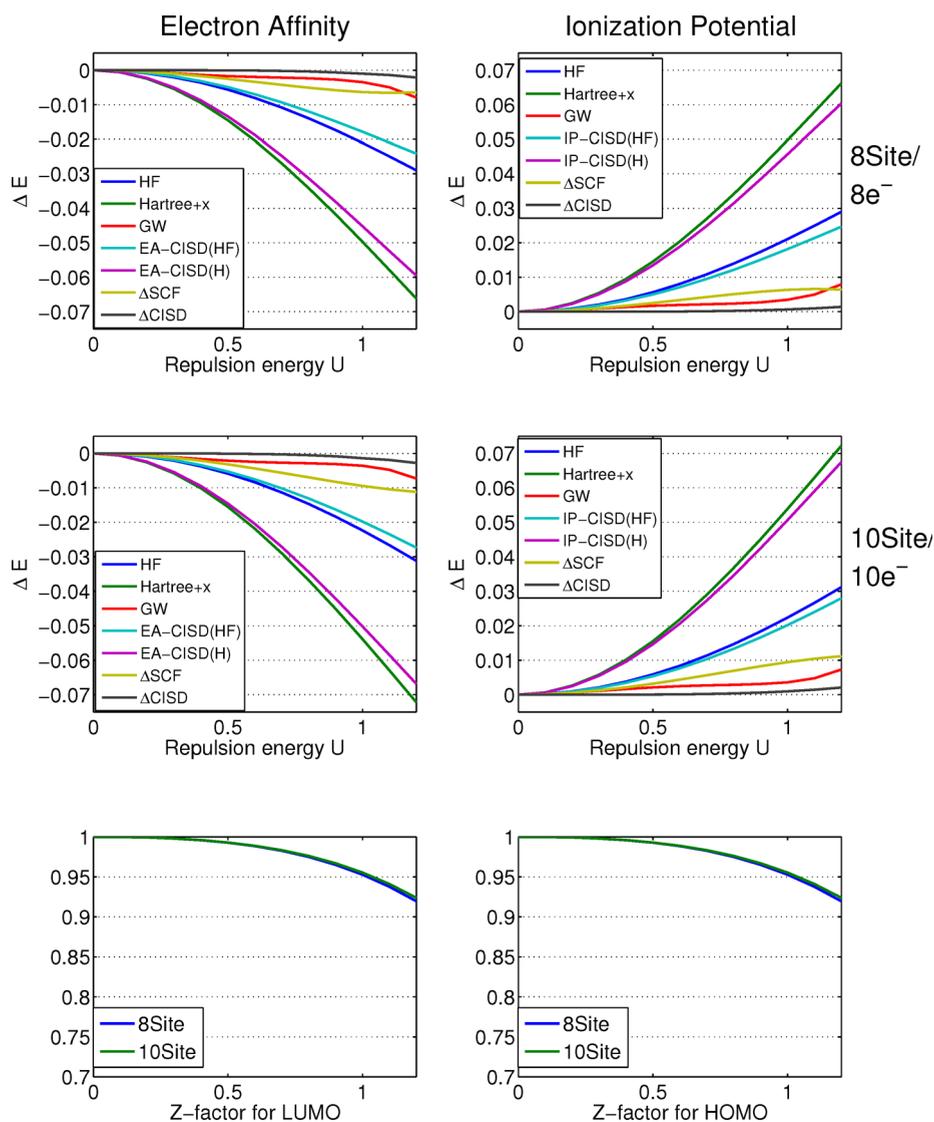
With this background in mind, in Figure 8 we plot the error electron affinity given by GW as a function of the number of singlet states included in the calculation for two different cases: (i) 8-Site/ $8e^-$  metallic system with  $U = 0.5$  and (ii) 8-Site/ $8e^-$  molecular system with  $U = 0.5$  and  $V_{\text{even}} = -2.0$ . On the one hand, for the metallic system, a strong GW correction can be obtained by including just one RPA excited state; for these systems and this  $U$  value, we find one low lying state that is reasonably separated energetically from higher excited states and yields a strong correction. On the other hand, for the molecular systems, the error decreased very slowly (almost linearly). In other words, one must include all RPA states to maintain the accuracy of the GW method for a molecular system.<sup>39,40</sup> Given the large cost of the full GW calculation, it will be interesting to compare relative (as opposed to absolute) ionization potentials and electron affinities for real molecules as a function of the number of states included. This work is ongoing.

Finally, a few words are in order about self-consistency. To avoid self-consistency, one can use eq 41. Alternatively, one can iterate the GW equations to satisfy eq 39. We have performed a simple eigenvalue self-consistent GW calculation (evGW)<sup>41</sup> and we find that results given by evGW are actually very close to our perturbative GW method with the linear expansion (eq 41). This success of the perturbative GW approximation is consistent with the fact that the  $Z$ -factor is very close to 1 (larger than 0.9) and validates the results presented in Figures 1–6.

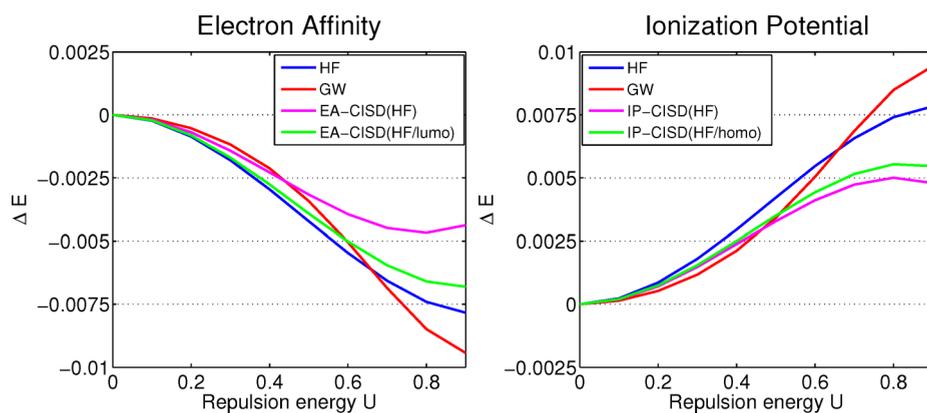
We have found, however, that the  $Z$ -factor values for orbitals other than HOMO and LUMO were usually far away from 1 with correspondingly large errors compared to exact attachment–detachment energies.

## V. CONCLUSION

In this paper, we have systematically compared the performance of GW against various wave-function-based methods for the calculation of ionization potentials and electronic affinities for several 1D Hubbard models. Three different types of systems



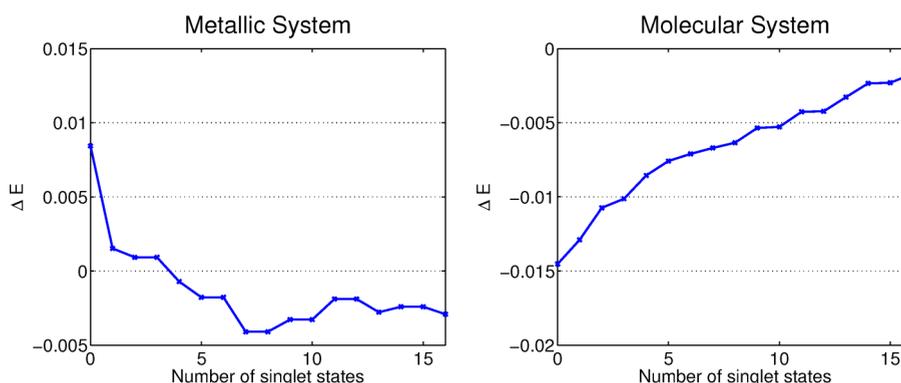
**Figure 6.** Errors for electron affinities and ionization potentials and the quasiparticle renormalization ( $Z$ ) factor for “molecular” Hubbard models ( $V_{\text{even}} = -2.0$ ,  $V_{\text{odd}} = 0$ ,  $\tau = 1.0$ ). All errors are relative to the exact diagonalization. Note that the GW method, though slightly worse than  $\Delta\text{CISD}$ , outperforms other methods even in this very insulating case.



**Figure 7.** Errors for electron affinities and ionization potentials for the 8-Site/ $8e^-$  molecular system ( $V_{\text{even}} = -1.0$ ). Results given by HF, IP/EA-CISD(HF), and GW are taken from Figure 5. Here we compare against IP-CISD(HF/homo) and EA-CISD(HF/lumo). Note that by freezing one orbital, the electron affinity changes significantly but the ionization potential does not.

have been studied: metallic, impurity, and molecular (semi-conducting/insulating) systems.

Although  $\Delta\text{CISD}$  gives almost exact results for all cases, the most striking conclusion from the data above is that the GW



**Figure 8.** Errors for electron affinities for 8-Site/ $8e^-$  metallic system ( $U = 0.5$ ) and molecular system ( $U = 0.5$ ,  $V_\mu = -2.0$ ) with respect to the number of singlet states included in the calculation (eq 32). Including no RPA states is the Hartree result, and including the maximum number of states gives the GW result. Note that, on the left panel, including the first excited RPA state yields a pretty good result whereas, on the right panel, all RPA states need to be included due to the slow convergence.

method surpasses other wave function methods in two extreme limits. On the one hand, for the metallic case with reasonably large  $U$ , GW performs significantly better than wave function methods (except  $\Delta$ CISD). On the other hand, for the molecular system with the largest HOMO/LUMO gap, GW also gives a very accurate result. For systems between these two extreme cases, the advantages of GW becomes less obvious and the wave-function-based methods behave better.

As DFT specialists may well appreciate, the Hartree approximation yields a small improvement over HF for both the impurity systems and molecular systems with small energy gaps ( $V_\mu \ll \tau$ ). For the insulator case with a large HOMO/LUMO gap, the Hartree approximation dramatically fails to make accurate predictions but can be used as a reasonable reference for GW. Altogether, these results emphasize the comparative advantages of the GW method versus traditional quantum chemistry approaches across a large range of Hamiltonians (even if GW is not always the optimal method). Looking forward, it is clear why GW is currently being applied to a variety of molecular systems.<sup>40,42–44</sup>

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### Notes

The authors declare no competing financial interest.

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