

# All-electron $GW$ methods implemented in molecular orbital space: Ionization energy and electron affinity of conjugated molecules

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An efficient all-electron  $G^0W^0$  method and a quasiparticle self-consistent  $GW$  (QSGW) method for molecules are proposed in the molecular-orbital space with the full random-phase approximation. The convergence with the basis set is examined. As an application, the ionization energy and electron affinity of a series of conjugated molecules (up to 32 atoms) are calculated and compared to the experiment. The QSGW result improves the  $G^0W^0$  result and both of them are in significantly better agreement with experimental data than those from Hartree-Fock (HF) and hybrid density-functional calculations, especially for electron affinity. The nearly correct energy gap and suppressed self-interaction error by the HF exchange make our method a good candidate for investigating electronic and transport properties of molecular systems.

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Density-functional theory (DFT) has become the most extensively used method for calculating the electronic structure of solids and molecules<sup>1</sup> because of its high efficiency and reasonable accuracy. Despite its success in describing ground-state electronic properties, DFT still faces big challenges for some applications due to intrinsic issues, such as the underestimated energy gap and self-interaction error (SIE), as in its practical scheme with the local-density approximation (LDA) or generalized gradient approximation (GGA). For example, in the calculation of molecular conductance<sup>2–4</sup> these issues will lead to an incorrect molecule-lead charge transfer, an incorrect position of the lead chemical potential in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as well as the broadening of the HOMO and LUMO, especially for weakly coupled systems,<sup>4</sup> causing a much overestimated molecular conductance, even by orders of magnitude in some cases.<sup>2,4</sup> This is in strong contrast with the success of DFT structural prediction for solids and molecules.

Physically, even an exact DFT calculation with a local exchange-correlation potential ( $V_{xc}$ ) cannot give a correct HOMO-LUMO gap due to the lack of the discontinuity. Improvement with a nonlocal  $V_{xc}$  is still under development and facing challenges.<sup>4–6</sup> Different from DFT, the Hartree-Fock (HF) method is SIE free and can usually give a reasonable HOMO energy (Koopmans' theorem) but lacks electron correlation and cannot predict a reasonable LUMO energy. Many-body quasiparticle calculation in the  $GW$  approximation<sup>7–9</sup> may provide a solution though its non-self-consistent version ( $G^0W^0$ ) is not a conserving approach and may be problematic to quantum transport calculations.<sup>10,11</sup> Additionally, its result is dependent on the initial input from DFT or HF. It also faces a challenging computational effort for large molecular systems.

In spite of these issues, the  $G^0W^0$  approach has been very successfully applied to the band-structure calculation for bulk semiconductors,<sup>12–14</sup> improving significantly the result of DFT. However, its applicability and accuracy for molecular systems is still an open problem,<sup>9,15–17</sup> considering the stronger electronic relaxation effect<sup>15</sup> and the weaker

screening, compared with the case of solids. Besides the physics, the ways of dealing with the core electrons and the convergence to the size of the basis set are technical factors also affecting its accuracy. For solids, the pseudopotential approach has been quite successful in ground-state electronic structure calculations, while for excited states its quality is still under debate. Some calculations show that the valence-core interaction is important and a full-potential all-electron treatment is required to evaluate the  $G^0W^0$  approximation for semiconductors,<sup>18</sup> while some other calculations show that the pseudopotential approximation can be quite safely applied to excited-state calculations for silicon and silicon carbide.<sup>19</sup> For molecules, recent work shows that the core electrons play an important role in determining accurately the molecular excitation energies (the effect is as much as 1 eV).<sup>9</sup>

Considering the success and the problems of the  $GW$  method and the difference between molecules and solids, it is interesting to apply the method to study molecular electronic properties and to see how well it works. In the light of the existing finding about the important role of core electrons,<sup>9</sup> an efficient *ab initio* all-electron  $GW$  approach being able to deal with large molecules is desirable. In this regard, a localized basis set has many more advantages than a nonlocalized basis set (for example, of plane waves) because of the difficulty of dealing with the core electrons. Furthermore, for molecular systems a localized basis set can achieve a much better computational efficiency, especially the Gaussian basis functions,<sup>20,21</sup> for which the two-electron integrals can be calculated analytically.

In this work, we first propose an efficient all-electron non-self-consistent  $G^0W^0$  method based on the full random-phase approximation (RPA) using Gaussian basis functions and a HF input. To achieve a higher computational efficiency, it is implemented in the molecular-orbital (MO) space with techniques for reducing the error coming from the incompleteness of the basis set. The correlation self-energy is determined first on the imaginary energy axis and then on the real energy axis using the analytical continuation approach which was proposed originally for a space-time approach.<sup>22,23</sup> The convergence

with respect to the size of the basis set is examined by calculating He and Be atoms using a series of basis sets.

To address the issue of initial input dependence with the  $G^0W^0$  approach, we further implement a quasiparticle self-consistent  $GW$  (QSGW) method,<sup>12,14,24</sup> in which a self-consistency is performed between the  $G^0W^0$  and a DFT-like calculation with a nonlocal  $V_{xc}$  constructed from the  $G^0W^0$  self-energy, producing an input-independent result. The converged  $V_{xc}$  may help to suppress the SIE in DFT since the real (nonlocal) exchange is used. As a real, hermitian, and energy-independent self-energy, it may also help to some extent with the conserving issue of the  $G^0W^0$  approach.

As an application of our methods, we investigate the ionization energy (IE) and electron affinity (EA) of a series of conjugated molecules. As is well known, conjugated molecules play the most important roles in molecular electronics because of their small HOMO-LUMO gap, good molecular conductance, and tunable electronic states. The systems studied include acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ), allene ( $C_3H_4$ ), diacetylene ( $C_4H_2$ ), benzene ( $C_6H_6$ ), phenylacetylene ( $C_8H_6$ ), naphthalene ( $C_{10}H_8$ ), biphenyl ( $C_{12}H_{10}$ ), anthracene ( $C_{14}H_{10}$ ), and perylene ( $C_{20}H_{12}$ ), for which reliable experimental data are available.<sup>25</sup> Comparison to the experimental data shows that our  $G^0W^0$  and QSGW results improve the HF ones significantly, especially for EA. The QSGW improves the  $G^0W^0$  further and shows a very good agreement between theory and experiment. This indicates that the *ab initio* all-electron  $GW$  calculation can describe very well molecular electronic structures. The computational efficiency of our methods makes it possible to easily deal with systems consisting of several tens of atoms from the first principles, making the QSGW approach a good candidate for investigating electronic and transport properties of molecular devices.

In the present implementation the  $GW$  self-energy is divided into a (energy-independent) bare-exchange part and a correlation part:  $\Sigma = \Sigma^x + \Sigma^c$ . We first work on the imaginary energy axis, on which the correlation part is

$$\begin{aligned} \Sigma^c(\mathbf{r}, \mathbf{r}'; i\omega) \\ = -\frac{1}{2\pi} \int_{-\infty}^{\infty} G[\mathbf{r}, \mathbf{r}', i(\omega + \omega')] W^c(\mathbf{r}, \mathbf{r}'; i\omega') d\omega', \end{aligned} \quad (1)$$

where  $G$  is the Green's function and  $W^c \equiv W - v$  is the screened Coulomb potential minus the bare Coulomb potential. The advantage of calculating the self-energy along the imaginary axis is that one can avoid the sharp pole structures in both  $G$  and  $W^c$ . In the MO space (the MOs are denoted by  $m, n, \dots$ ) the Green's function simply reads

$$G_{mn}(i\omega) = \frac{\delta_{mn}}{i\omega - \epsilon_n}, \quad (2)$$

due to the orthonormality of the MOs. Here  $\epsilon_n$  denotes the  $n$ th eigenvalue and the Fermi energy is set by  $\omega = 0$ :

$$W_{mn}^c(i\omega) = [\epsilon^{-1}(i\omega)v]_{mn} - v_{mn}, \quad (3)$$

where  $v_{mn}$  is the two-center Coulomb integral and  $\epsilon(i\omega)$  is the dielectric function matrix which is calculated by

$$\epsilon_{mn}(i\omega) = I_{mn} - [P(i\omega)v]_{mn}, \quad (4)$$

with  $I$  being identity matrix and  $P$  the polarization function which can be determined by RPA:

$$P(\mathbf{r}, \mathbf{r}'; i\omega) = 2 \sum_{kl} (f_k - f_l) \frac{\psi_k(\mathbf{r})\psi_l^*(\mathbf{r}')\psi_l(\mathbf{r}')\psi_k^*(\mathbf{r})}{i\omega - (\epsilon_l - \epsilon_k)}, \quad (5)$$

where  $f$  is the occupation number and  $\psi$  are the MOs. If the MO space is complete,  $P$  can be expressed as

$$P_{mn}(i\omega) = 2 \sum_{kl} \frac{f_k - f_l}{\epsilon_l - \epsilon_k - i\omega} O_m^{kl} O_n^{kl}, \quad (6)$$

in terms of the three-center overlap integrals of the MOs:

$$O_m^{kl} \equiv \int d^3\mathbf{r} \psi_m(\mathbf{r})\psi_k(\mathbf{r})\psi_l(\mathbf{r}). \quad (7)$$

However, in practice, the incompleteness of the MO space will cause an error in the calculation of  $P$  and, even worse, causes a larger error in the product of  $Pv$ . To suppress this error, we avoid the individual calculations of  $P(i\omega)$  and  $v$  matrices but calculate the product as a whole in terms of the electron integrals:

$$[P(i\omega)v]_{mn} = 2 \sum_{kl} \frac{f_k - f_l}{\epsilon_l - \epsilon_k - i\omega} O_m^{kl} C_n^{kl}, \quad (8)$$

where

$$C_n^{kl} \equiv \iint d^3\mathbf{r} d^3\mathbf{r}' \frac{\psi_n(\mathbf{r})\psi_k(\mathbf{r}')\psi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

are the three-center Coulomb integrals of the MOs. The two kinds of three-center MO integrals are determined in terms of the corresponding three-center integrals of the atomic orbitals presented by the standard contracted Gaussian basis functions, which can then be calculated analytically. In this way, the error coming from the incompleteness of the MO space in the calculation of the dielectric function can be suppressed. However, in the calculation of the  $W^c(i\omega)$  matrix in Eq. (3), the two-center Coulomb integral matrix  $v$  and its product with  $\epsilon^{-1}(i\omega)$  are still needed. To avoid this, we define

$$\tilde{W}^c(i\omega) \equiv [I - P(i\omega)v]^{-1} - I, \quad (10)$$

and therefore

$$W^c(i\omega) = \tilde{W}^c(i\omega)v. \quad (11)$$

After expanding Eq. (1) in the MO space and substituting Eq. (2) for  $G(i\omega)$  we have

$$\Sigma_{mn}^c(i\omega) = -\frac{1}{2\pi} \sum_{jkl} O_m^{kj} O_n^{jl} \int_{-\infty}^{\infty} \frac{W_{kl}^c(i\omega')}{i(\omega + \omega') - \epsilon_j} d\omega'. \quad (12)$$

Substituting Eq. (11) for  $W^c(i\omega)$  leads to

$$\begin{aligned} \Sigma_{mn}^c(i\omega) = & -\frac{1}{2\pi} \sum_{jk'l'} O_m^{kj} \sum_l (v_{l'l} O_n^{lj}) \\ & \times \int_{-\infty}^{\infty} \frac{\tilde{W}_{kl'}^c(i\omega')}{i(\omega + \omega') - \epsilon_j} d\omega'. \end{aligned} \quad (13)$$

By making use of the orthonormality of the MOs we get the final expression for  $\Sigma^c$ :

$$\Sigma_{mn}^c(i\omega) = -\frac{1}{2\pi} \sum_{jkl} O_k^{mj} C_l^{jn} \times \int_{-\infty}^{\infty} \frac{\tilde{W}_{kl}^c(i\omega')}{i(\omega + \omega') - \epsilon_j} d\omega' \quad (14)$$

$$\equiv -\frac{1}{2\pi} \sum_{jkl} O_k^{mj} \mathcal{W}_{jkl}(i\omega) C_l^{jn}. \quad (15)$$

The result is simply a product of the three three-dimensional arrays, involving only the three-center overlap matrix and the three-center Coulomb matrix without any individual calculations of  $P$  and  $v$ . The integral  $\mathcal{W}_{jkl}$  can be calculated by the Gaussian quadrature. Because  $\tilde{W}^c$  varies extremely smoothly as a function of  $\omega$ , very few energy grids (about 100 points from 0 to  $\infty$ ) are usually needed to well converge the elements of  $\mathcal{W}$ . In practice, the integration of  $\tilde{W}^c(i\omega')$  shares the energy grids for calculating  $\Sigma^c(i\omega)$  ( $N_\Sigma$  points from 0 to  $E_\Sigma$ ) plus additional  $N_w$  points from  $E_\Sigma$  to  $\infty$ . The typical value for  $E_\Sigma$  is 300 eV, and  $N_\Sigma \sim 100$  and  $N_w \sim 20$  are found good enough to well converge the result. We would like to mention that, at first glance, Eq. (15) suggests an  $O(N^5)$  scaling with the number of atoms  $N$  for a given basis set. However, we can rearrange the summation in the following order:

$$\sum_j \left[ \sum_k O_k^{mj} \left( \sum_l \mathcal{W}_{jkl} C_l^{jn} \right) \right]. \quad (16)$$

In this way, matrix multiplication in each step will scale as  $O(N^4)$  and, therefore, an overall  $O(N^4)$  scaling can be achieved for the full  $\Sigma^c(i\omega)$  matrix.

After having obtained  $\Sigma^c$  on the imaginary energy axis, we determine its values on the real energy axis using the analytical continuation approach,<sup>22,23</sup> and we least-square fit each element to the multipole form using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization technique:

$$a_0 + \sum_{j=1}^n \frac{a_j}{\omega - b_j}, \quad (17)$$

with complex parameters  $a_j$  and  $b_j$ . For bulk semiconductors it was found that  $n = 2$  is usually good enough.<sup>22,23</sup> For molecules, however, we find that  $n = 6$  is generally required to give an extremely stable and accurate fitting. Our computational code has been parallelized using a message passing interface in two steps: The computation of  $\mathcal{W}(i\omega)$  and  $\Sigma^c(i\omega)$  is parallelized on the energy grids and the computation of the BFGS fitting is parallelized on the MOs.

To address the issues with the  $G^0W^0$  method, we implement a QSGW approach, in which the  $G^0W^0$  self-energy is used to construct a nonlocal real exchange-correlation potential  $V_{xc}$  for a DFT-like calculation. In practice, we follow the scheme proposed in Refs. 12,14, and 24, which has been shown to be very successful for bulk semiconductors but is now implemented in the MO space for molecules:

$$[V_{xc}]_{mn} = \text{Re}[\Sigma^c(\epsilon_m) + \Sigma^c(\epsilon_n)]_{mn}/2 + \Sigma_{mn}^x, \quad (18)$$

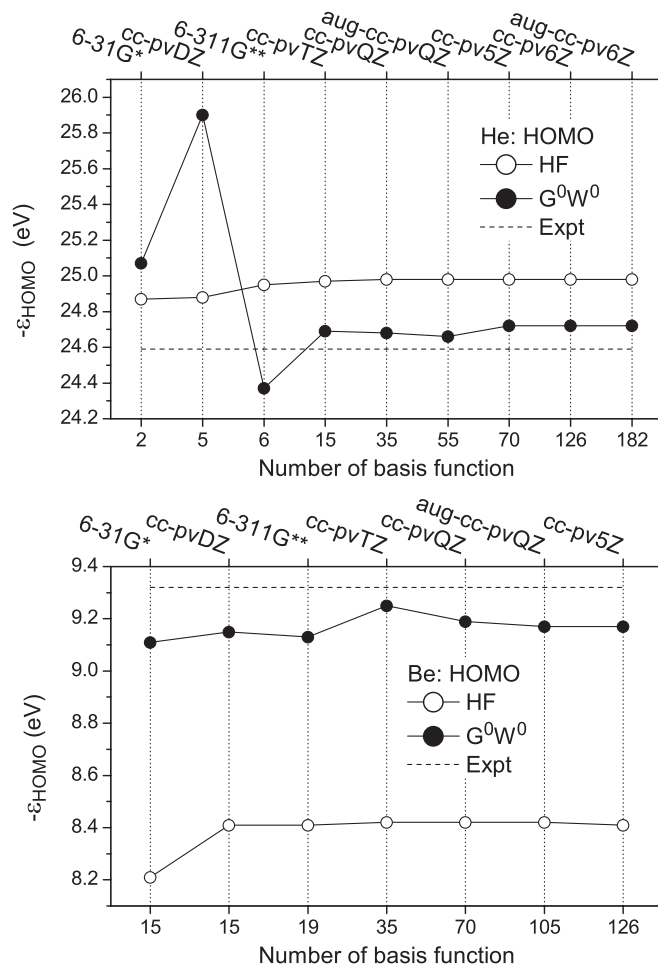


FIG. 1. Dependence of the  $-\epsilon_{\text{HOMO}}$  of the He atom (upper panel) and Be atom (lower panel) on the size of the basis set used in the HF and  $G^0W^0$  calculations. The experimental result of IE is shown by the horizontal dashed line.

with  $\Sigma^x$  being calculated in terms of the HF exchange operator. The DFT-like calculation will generate new eigenvalues and MOs which can be used for the next  $G^0W^0$  calculation. This procedure continues until the maximum change in the  $V_{xc}$  elements is smaller than the convergence criteria adopted. Previously, the QSGW approach implemented using the full-potential linear muffin-tin orbital method was applied to bulk semiconductors and improved significantly the  $G^0W^0$  band gaps.<sup>12,24</sup> For molecules, its applicability and quality are still unknown.

Like other correlated electronic structure methods (for instance, the second-order Møller-Plesset theory and the coupled-cluster method) the  $G^0W^0$  method is more sensitive to the size of the basis set than DFT and HF methods. So far, careful examinations for convergence behavior are still lacking in the literature,<sup>9</sup> probably leading to the scattering results from different calculations and biased conclusions for different systems. To examine the basis-set convergence of our method, we first calculate the minus-HOMO energy  $-\epsilon_{\text{HOMO}}$ , i.e., IE, of He and Be atoms, adopting a series of different basis sets:<sup>26</sup> 6-31G\*, 6-311G\*\*, cc-pvDZ, cc-pvTZ, cc-pvQZ, aug-cc-pvQZ, cc-pv5Z, cc-pv6Z, and aug-cc-pv6Z, and we plot the results in Fig. 1.

TABLE I. Calculated (cc-pVTZ level) and experimental results of IE and EA (in eV) of ten conjugated molecules, as well as their charge-induced relaxation energies  $\Delta E^+$  and  $\Delta E^-$ . The experimental data are cited from Ref. 25.

Molecules	IE								EA							
	$\Delta E^+$	$G^0W^0$	QSGW	HF	$\Delta HF$	B3LYP	$\Delta B3LYP$	Expt.	$\Delta E^-$	$G^0W^0$	QSGW	HF	$\Delta HF$	B3LYP	$\Delta B3LYP$	Expt.
C <sub>2</sub> H <sub>2</sub>	0.11	11.44	11.31	11.07	9.69	8.05	11.26	11.40								
C <sub>2</sub> H <sub>4</sub>	0.19	10.50	10.53	10.10	8.74	6.60	10.39	10.51								
C <sub>3</sub> H <sub>4</sub>	0.57	9.95	9.78	9.74	8.24	6.91	9.51	9.69								
C <sub>4</sub> H <sub>2</sub>	0.09	10.34	10.12	9.98	8.72	7.35	9.85	10.17								
C <sub>6</sub> H <sub>6</sub>	0.14	9.28	9.20	9.00	7.73	6.90	9.11	9.24								
C <sub>8</sub> H <sub>6</sub>	0.12	8.94	8.66	8.60	8.50	6.54	8.50	8.82								
C <sub>10</sub> H <sub>8</sub>	0.09	8.16	8.07	7.78	6.82	6.02	7.85	8.14	0.12	-0.60	-0.34	-1.35	-2.17	1.46	-0.32	-0.20
C <sub>12</sub> H <sub>10</sub>	0.30	8.31	8.21	8.03	6.77	6.16	7.81	8.16	0.44	-0.66	-0.29	-1.38	-2.30	1.39	-0.36	0.13
C <sub>14</sub> H <sub>10</sub>	0.07	7.42	7.27	6.97	6.04	5.47	7.04	7.44	0.10	0.23	0.37	-0.51	-1.33	2.08	0.42	0.53
C <sub>20</sub> H <sub>12</sub>	0.08	6.94	6.77	6.50	5.19	5.17	6.58	6.96	0.09	0.65	0.91	0.13	-0.90	2.33	0.84	0.97

For the He atom, the 6-31G\*, cc-pvDZ, and 6-311G\*\* basis sets have only 2, 5, and 6 basis functions, respectively. For such small basis sets the  $G^0W^0 - \epsilon_{\text{HOMO}}$  fluctuates remarkably. However, once the basis set is larger than 15 basis functions the results of both He and Be atoms tend to be well converged and the fluctuation is around 0.1 eV. The important thing is that for both atoms the  $G^0W^0$  result improves significantly the HF result: For He the  $-\epsilon_{\text{HOMO}}$  is corrected downward while for Be it is corrected upward, becoming much closer to the experimental data.

The IE or EA of a molecule includes two contributions, i.e., the vertical IE or EA and the corresponding charge-induced structural relaxation energy ( $\Delta E^+$  or  $\Delta E^-$ ):  $\text{IE} = (\text{IE})_{\text{vert.}} - \Delta E^+$  and  $\text{EA} = (\text{EA})_{\text{vert.}} + \Delta E^-$ .  $\Delta E^{\pm}$  can be determined by performing a structural relaxation calculation with the charge. For the ten conjugated molecules studied in this work we first optimize their structures on the DFT/B3LYP/cc-pVTZ level and then calculate their  $\Delta E^+$  and  $\Delta E^-$  by allowing further relaxation with the charge. From the results listed in Table I one can see that  $\Delta E^+$  is comparable with  $\Delta E^-$  and their values depend strongly on the molecular structure.

The results of IE and EA of the ten conjugated molecules given by the different methods are listed in Table I together

with the available experimental data cited from Ref. 25. For EA only the four largest molecules are studied, which have a positive or nearly zero experimental value. The other molecules are too small to have a positive value of EA because the added electron is unbound, and therefore they are not studied. The results are also plotted in Fig. 2 for a better view and comparison.

For molecular systems the hybrid DFT/B3LYP has been proven to be a significant improvement to DFT/LDA and DFT/GGA because the HF exchange is partly included, suppressing partly the SIE with LDA and GGA.<sup>4</sup> However, as shown in Table I and Fig. 2, the results of IE and EA of the conjugated molecules are still far from being correct. In spite of lacking an electron correlation, the HF method gives a much better result of IE due to the Koopmans' theorem, but its result of EA is very bad, being comparable to the B3LYP result but with an opposite trend (see Fig. 2).

For a molecule with  $N$  electrons, its IE and EA can be explicitly determined by a total-energy-difference calculation (i.e., the  $\Delta\text{SCF}$  calculation):<sup>27</sup>

$$\text{IE} = E_{\text{total}}(N-1) - E_{\text{total}}(N), \quad (19)$$

$$\text{EA} = E_{\text{total}}(N) - E_{\text{total}}(N+1).$$

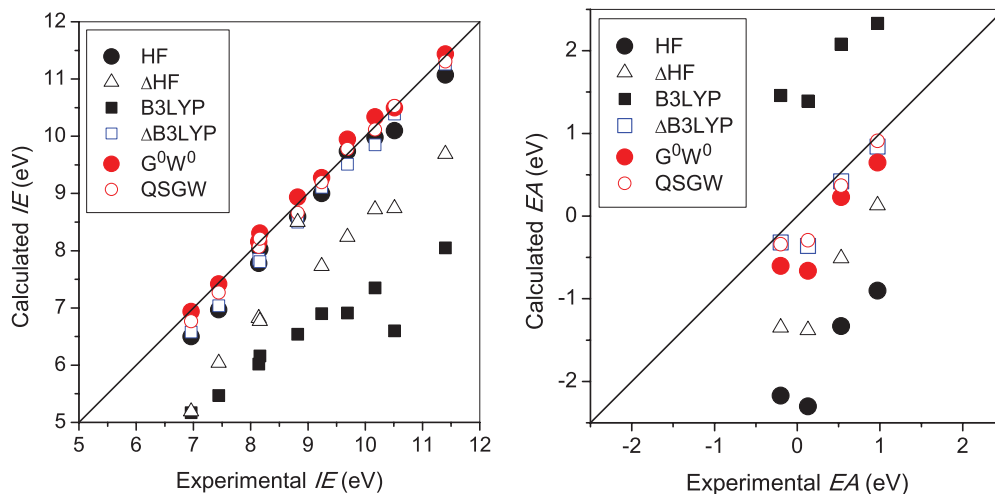


FIG. 2. (Color online) Comparison between the calculated results and experimental data of the IE and EA of the ten conjugated molecules in Table I.

The accuracy will depend on the quality of the total energies  $E_{\text{total}}$ . One can see in Table I and Fig. 2 that the  $\Delta\text{SCF}$  calculation using HF ( $\Delta\text{HF}$ ) improves HF for EA considerably but the  $\Delta\text{HF}$  result of IE becomes much worse because of the inaccurate total energy (a correlation is absent). On the other hand, the  $\Delta\text{SCF}$  calculation using B3LYP ( $\Delta\text{B3LYP}$ ) gives very good results of both IE and EA because of its accurate total energy.

The  $G^0W^0$  result improves the HF result considerably for IE and significantly for EA, showing that the correlation is more important for the excited states. The QSGW result improves the  $G^0W^0$  result further, being in very good agreement with the available experimental data<sup>25</sup> and the  $\Delta\text{B3LYP}$  result. This finding is consistent with previous calculations<sup>12,14,24</sup> which showed a significant improvement from QSGW to  $G^0W^0$  for fundamental band gaps in bulk semiconductors.

In a very recent  $GW$  calculation for molecules using Gaussian basis functions<sup>20</sup> it was found that a simple self-consistency on eigenvalues can improve significantly the  $G^0W^0/\text{LDA}$  result, probably because the input eigenvalues from DFT/LDA are very poor. Interestingly, this improvement was found to be almost equivalent to a  $G^0W^0/\text{HF}$  calculation. This finding is consistent with our result that the  $G^0W^0/\text{HF}$  calculation can give quite good results for molecules. However, our work shows that the self-consistency over  $G^0W^0/\text{HF}$  (on both eigenvalues and eigenfunctions) in the QSGW approach can improve further the  $G^0W^0/\text{HF}$  result, implying that the self-consistency on the eigenfunctions has also some effect.

Overall, our work shows that the all-electron *ab initio*  $G^0W^0$  and QSGW methods can describe very well the electronic structures of conjugated molecules, as indicated by the good agreement between theory and experiment. Furthermore, the very good agreement between our QSGW result and the  $\Delta\text{B3LYP}$  one confirms further the validity of the former because the electron-removal- and electron-addition-induced electronic relaxations are fully included in the latter. Our finding is consistent with a recent work of *ab initio*  $G^0W^0$  calculation for small molecules,<sup>9</sup> which showed that the inclusion of a core-valence interaction is important in obtaining accurate excitation energies, but

different from a very recent work of a  $\pi$ -only model  $GW$  calculation<sup>15</sup> which found, however, that the accuracy of the  $GW$  method is largely limited by the electronic relaxation. This discrepancy in the conclusion may be understood by considering the role played by the  $\sigma$  states which have a much broader energy range. Physically, the lower dimensionality of molecules causes much more localized electronic states which will lead to a much stronger electronic relaxation effect than in solids. Consequently, for conjugate molecules an accurate description not only for the valence  $\sigma$  states (and therefore the resulting  $\pi$ - $\sigma$  relaxation) but also for the core electrons may become important.

In summary, we have proposed an efficient non-self-consistent  $G^0W^0$  method which is based on the full RPA and implemented in the molecular-orbital space with techniques for reducing the error coming from the incompleteness of the basis set. The convergence of its result with regard to the size of the basis set has been examined. Based on this, we have further implemented a QSGW approach with Gaussian basis functions. The high computational efficiency allows us to deal with larger molecules, and we have applied our methods to calculate the ionization energy and electron affinity of ten conjugated molecules with up to 32 atoms. The  $G^0W^0$  result improves the HF result significantly, especially for EA, and, furthermore, the QSGW improves the  $G^0W^0$  and gives results of both IE and EA in very good agreement with the available experimental data and also with the results from the  $\Delta\text{SCF}$  calculation using the B3LYP functional. This indicates that our all-electron *ab initio*  $GW$  calculation can describe very well molecular electronic structures, making the QSGW approach a good candidate for investigating electronic and transport properties of molecular devices.

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