

assessment of the GW approximation itself.

Here we report on single-shot  $G_0W_0$  and fully self-consistent GW calculations of QP energies for a set of 33 molecules. The calculated IPs are compared with experimental values as well as single-particle eigenvalues obtained from Hartree-Fock and DFT-PBE/PBE0 theories. As additional benchmarks we compare to second-order Möller-Plesset (MP2) and DFT-PBE total energy differences between the neutral and cation species. Special attention is paid to the effect of selfconsistency in the GW self-energy and the role of the initial Green function,  $G_0$ , used in one-shot  $G_0W_0$  calculations. The use of PAW rather than pseudopotentials facilitate the inclusion of core-valence exchange, which we find can contribute significantly to the HF and GW energies. Our results show that the GW approximation yields accurate single-particle excitation energies for small molecules improving both hybrid DFT and full Hartree-Fock results.

The paper is organized as follows. In Sec. II we describe the theoretical and numerical details behind the GW calculations, including the augmented Wannier function basis set, the self-consistent solution of the Dyson equation, and the evaluation of valence-core exchange within PAW. In Sec. III we discuss and compare the results of  $G_0W_0$ , GW, HF, PBE0, and PBE calculations. We analyze the role of dynamical screening, and discuss the effect of self-consistency in the GW self-energy. We conclude in Sec. IV.

## II. METHOD

### A. Augmented Wannier function basis

For the GW calculations we apply a basis set consisting of projected Wannier functions (PWF) augmented by numerical atomic orbitals (NAO). The PWFs,  $\phi_i$ , are obtained by maximizing their projections onto a set of target NAOs,  $\Phi_{Alm}$ , subject to the condition that they span the set of occupied eigenstates,  $\psi_n$ . Thus we maximize the functional

$$\Omega = \sum_i \sum_{A,l,m} |\langle \phi_i | \Phi_{Alm} \rangle|^2 \quad (1)$$

subject to the condition  $\text{span}\{\phi_i\} \supseteq \text{span}\{\psi_n\}_{\text{occ}}$  as described in Ref. 44. The target NAOs are given by  $\Phi_{Alm}(\mathbf{r}) = \zeta_{Al}(r)Y_{lm}(\mathbf{r})$  where  $\zeta_{Al}$  is a modified Gaussian which vanish outside a specified cut-off radius, and  $Y_{lm}$  are the spherical harmonics corresponding to the valence of atom  $A$ . The number of PWFs equals the number of target NAOs. For example we obtain one PWF for H ( $l_{\text{max}} = 0$ ), and four PWFs for C ( $l_{\text{max}} = 1$ ). The PWFs mimic the target atomic orbitals but in addition they allow for an *exact* representation of all the occupied molecular eigenstates. The latter are obtained from an accurate real-space PAW-PBE calculation<sup>45,46</sup>.

The PWFs obtained in this way provide an exact representation of the occupied PBE eigenstates. However,

this does not suffice for GW calculations because the polarizability,  $P$ , and the screened interaction,  $W$ , do not live in this subspace. Hence we augment the PWFs by additional NAOs including so-called polarization functions which have  $l = l_{\text{max}} + 1$  and/or extra radial functions (zeta functions) for the valence atomic orbitals. For more details on the definition of polarization- and higher zeta functions we refer to Ref. 46. To give an example, a double-zeta-polarized (DZP) basis consists of the PWFs augmented by one set of NAOs corresponding to  $l = 0, \dots, l_{\text{max}}$  and one set of polarization orbitals. Note that the notation, SZ, SZP, DZ, DZP, etc., is normally used for pure NAO basis sets, but here we use it to denote our augmented Wannier basis set. We find that the augmented Wannier basis is significantly better for HF and GW calculations than the corresponding pure NAO basis.

The GW and HF calculations presented in Sec. III were performed using a DZP augmented Wannier basis. This gives a total of 5 basis functions per H, Li, and Na, and 13 basis functions for all other chemical elements considered. In Sec. III C we discuss convergence of the GW calculations with respect to the size of the augmented Wannier basis.

### B. GW calculations

The HF and GW calculations for isolated molecules are performed using a Green function code developed for quantum transport.<sup>47</sup> In principle, this scheme is designed for a molecule connected to two electrodes with different chemical potentials  $\mu_L$  and  $\mu_R$ . However, the case of an isolated molecule can be treated as a special case by setting  $\mu_L = \mu_R = \mu$  and modelling the coupling to electrodes by a constant imaginary self-energy,  $\Sigma_{L/R} = i\eta$ . The chemical potential  $\mu$  is chosen to lie in the HOMO-LUMO gap of the molecule and the size of  $\eta$ , which provides an artificial broadening of the discrete levels, is reduced until the results have converged. In this limit of small  $\eta$  the result of the GW calculation becomes independent of the precise position of  $\mu$  inside the gap.

In Ref. 47 the GW-transport scheme was described for the case of an orthogonal basis set and for a truncated, two-index Coulomb interaction. Below we generalize the relevant equations to the case of a non-orthogonal basis and a full four-index Coulomb interaction. Some central results of many-body perturbation theory in a non-orthogonal basis can be found in Ref. 48.

The central object is the retarded Green function,  $G^r$ ,

$$G^r(\varepsilon) = [(\varepsilon + i\eta)S - H_{\text{KS}} + v_{\text{xc}} - \Delta v_{\text{H}} - \Sigma_{\text{xc}}^r[G](\varepsilon)]^{-1} \quad (2)$$

In this equation all quantities are matrices in the augmented Wannier basis, e.g.  $H_{\text{KS},ij} = \langle \phi_i | \hat{H}_{\text{KS}} | \phi_j \rangle$  is the KS Hamiltonian matrix and  $S_{ij} = \langle \phi_i | \phi_j \rangle$  is an overlap matrix. The term  $\Delta v_{\text{H}}$  represents the change in the Hartree potential relative to the DFT Hartree potential already contained in  $H_{\text{KS}}$ , see Appendix A.