Simple Approximate Physical Orbitals for *GW* Quasiparticle Calculations

Georgy Samsonidze, Manish Jain, Jack Deslippe, Marvin L. Cohen, and Steven G. Louie

Department of Physics, University of California, Berkeley, California 94720, USA
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

Generating unoccupied orbitals within density functional theory (DFT) for use in *GW* calculations of quasiparticle energies becomes prohibitive for large systems. We show that, without any loss of accuracy, the unoccupied orbitals may be replaced by a set of simple approximate physical orbitals made from appropriately prepared plane waves and localized basis DFT orbitals that represent the continuum and resonant states of the system, respectively. This approach allows for accurate quasiparticle calculations using only a very small number of unoccupied DFT orbitals, resulting in an order of magnitude gain in speed.

The *GW* approximation to the electron self energy is a proven and prominent method for treating the excited-state properties of solids from first principles [1,2]. The perturbative *GW* approach applied as a first-order correction to the Kohn-Sham density functional theory (DFT) eigenvalues (known as the G_0W_0 approximation) provides accurate quasiparticle energies in wide classes of materials [2–4]. Several recent efforts have been taken to extend the *GW* methodology beyond the standard G_0W_0 level such as the use of different mean-field starting points beyond DFT [5–7] and various levels of self-consistency [6,8].

For large systems with more than several hundred atoms, the *GW* calculations become quite challenging numerically. The expressions for the irreducible polarizability χ^0 and the self-energy Σ involve infinite summations over unoccupied single-particle orbitals of a mean-field starting Hamiltonian [2]. In practical calculations, these summations are truncated above a certain energy in the single-particle spectrum, but the number of unoccupied orbitals required increases rapidly with the system size for a convergent basis set. There have been proposals to avoid the explicit summation over unoccupied orbitals. These include the self-consistent linear-response Sternheimer approach [9,10], the extrapolar approximation [11], and the effective-energy technique [12] based on a common-energy-denominator approximation, the static remainder correction to Σ [13,14], and substitution of high-energy orbitals with just plane waves [15,16].

In this Letter, we report a method for constructing simple approximate physical orbitals (SAPOs) for use in *GW* calculations. The advantage of this approach is that it is compatible with standard *GW* methodology and therefore requires no modification of existing *GW* codes. We discuss our new method here within the framework of plane-wave pseudopotential calculations; however, it can be extended to other first-principles electronic structure methods straightforwardly. The form chosen for the SAPOs to replace DFT orbitals above a certain energy is based on the following physical motivation. In molecular systems, the spectrum of the electron single-particle orbitals is composed of bound, resonant, and continuum states. In extended systems, the distinctions among them are blurred, but these classifications are still useful. The continuum orbitals are constructed from linear combinations of plane waves that obey the symmetry of the system. The plane waves are defined as $\exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]$ where $\mathbf{k}$ is the reduced wave vector in the first Brillouin zone, $\mathbf{G}$ is the reciprocal lattice vector, and $\mathbf{r}$ is the position. The symmetrization of plane waves improves numerical stability in cutting off summations over unoccupied orbitals. The energy eigenvalues of the continuum orbitals are set to $\varepsilon_{n\mathbf{k}} = \langle V_{\mathrm{DFT}} \rangle + (\mathbf{k} + \mathbf{G})^2$ where $\langle V_{\mathrm{DFT}} \rangle$ is the averaged DFT potential, $(\mathbf{k} + \mathbf{G})^2$ are the kinetic energies of plane waves in Rydberg atomic units, and n is the index of $\mathbf{G}$-vectors sorted by kinetic energy. These energy eigenvalues, as discussed below, will need to be corrected further. A small number of resonant orbitals is obtained from a separate DFT calculation performed with limited short-range localized basis functions using methods such as SIESTA [17,18]. The energy eigenvalues resulting from the SIESTA calculation are shifted by matching the energy of the highest occupied molecular orbital (HOMO) to that obtained from a plane wave DFT calculation. This yields the energies $\varepsilon_{n\mathbf{k}}$ of the resonant orbitals, which again will be corrected further. Only the unoccupied orbitals are retained.

The approximate continuum and resonant orbitals and the subspace of the exact DFT orbitals (which in general contains all the occupied orbitals and a few unoccupied ones) form an overcomplete set of orbitals $\{\psi_{n\mathbf{k}}(\mathbf{r})\}$ (where n is the orbital number). As a result, the long-wavelength limit of the plane-wave matrix elements

$$\langle \psi_{n\mathbf{k}} | \exp[i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] | \psi_{m\mathbf{k}'} \rangle \underset{\mathbf{q}+\mathbf{G}\to 0}{\longrightarrow} \delta_{nm} \qquad (1)$$

(where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$) does not hold. This leads to errors in the head and wings of $\chi^0_{\mathbf{GG}'}(\mathbf{q} = \mathbf{0})$. To eliminate these

errors, we sort the approximate continuum and resonant orbitals and the subspace of exact DFT orbitals by energy eigenvalues $\{\varepsilon_{n\mathbf{k}}\}$ and apply the Gram-Schmidt orthonormalization in ascending order of $\varepsilon_{n\mathbf{k}}$:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \frac{\psi_{n\mathbf{k}}(\mathbf{r}) - \sum_{m=1}^{n-1}\langle\Psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle\Psi_{m\mathbf{k}}(\mathbf{r})}{\sqrt{1 - \sum_{m=1}^{n-1}|\langle\Psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle|^2}}. \quad (2)$$

We note that the exact DFT orbitals do not change with this procedure, only the approximate continuum and resonant orbitals are affected.

The unoccupied energies $\varepsilon_{n\mathbf{k}}$ described above are now not the correct eigenvalues for the new orbitals $\Psi_{n\mathbf{k}}(\mathbf{r})$. We make the correction to $\varepsilon_{n\mathbf{k}}$ by assuming that the energies $\varepsilon_{n\mathbf{k}}$ are the expectation values of the DFT Hamiltonian H for the old orbitals $\psi_{n\mathbf{k}}(\mathbf{r})$ and that the new orbitals $\Psi_{n\mathbf{k}}(\mathbf{r})$ are the eigenvectors of H with the eigenvalues $E_{n\mathbf{k}}$:

$$\langle\psi_{n\mathbf{k}}|H|\psi_{n\mathbf{k}}\rangle = \varepsilon_{n\mathbf{k}}, \qquad H\Psi_{n\mathbf{k}} = E_{n\mathbf{k}}\Psi_{n\mathbf{k}}. \quad (3)$$

With the help of Eqs. (2) and (3), we derive the following expression for the eigenvalues:

$$E_{n\mathbf{k}} = \langle\Psi_{n\mathbf{k}}|H|\Psi_{n\mathbf{k}}\rangle$$
$$= \varepsilon_{n\mathbf{k}} + \frac{\sum_{m=1}^{n-1}|\langle\Psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle|^2(\varepsilon_{n\mathbf{k}} - E_{m\mathbf{k}})}{1 - \sum_{m=1}^{n-1}|\langle\Psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle|^2}. \quad (4)$$

Instead of using Eq. (4), the DFT Hamiltonian H can be diagonalized in the basis of $\{\Psi_{n\mathbf{k}}(\mathbf{r})\}$ orbitals:

$$\sum_{m=1}^{N}\langle\Psi_{n\mathbf{k}}|H|\Psi_{m\mathbf{k}}\rangle C_{m\mathbf{k}}^{\ell} = \mathcal{E}_{\ell\mathbf{k}}C_{n\mathbf{k}}^{\ell},$$
$$\Phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{m=1}^{N}C_{m\mathbf{k}}^{n}\Psi_{m\mathbf{k}}(\mathbf{r}) \quad (5)$$

(where N is the total number of orbitals, which in general is much smaller than the number of plane waves in the DFT calculation) yielding more accurate energies $\mathcal{E}_{n\mathbf{k}}$ and orbitals $\Phi_{n\mathbf{k}}(\mathbf{r})$. The two sets $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$ and $\{\mathcal{E}_{n\mathbf{k}}, \Phi_{n\mathbf{k}}(\mathbf{r})\}$ are what we called the SAPOs.

We shall now verify the accuracy and efficiency of the SAPOs by performing G_0W_0 calculations with the BERKELEYGW package [19]. We first consider the benzene molecule C_6H_6 in a supercell calculation. The DFT calculation for benzene was done using the plane-wave pseudopotential code PARATEC [20]. We employ norm-conserving pseudopotentials [21] in nonlocal separable form [22], and use the local density approximation [23] for the exchange-correlation potential. The kinetic energy cutoffs for the plane-wave expansions of wave functions and the dielectric function are chosen to be $E_{\psi} = 60$ Ry and $E_{\epsilon} = 6$ Ry, respectively. The Coulomb potential is truncated at the faces of the supercell to avoid spurious interactions between periodic replicas of the benzene [24]. To retain the Coulomb interaction within the same benzene molecule, the size of the unit cell is set to $28.3 \times 25.9 \times 14.5\ a_0$ (where

a_0 is the Bohr radius). This is 8 times $(2 \times 2 \times 2)$ the size of the box confining the isosurface that encloses 99% of the electron density of benzene. To get the absolute orbital energies relative to the vacuum level, we subtract from DFT eigenvalues the electrostatic (ionic and Hartree) potential averaged on the faces of the supercell, $\langle V_i + V_H \rangle = 0.42$ eV. The resonant orbitals are calculated independently with SIESTA using the double-ζ polarized basis set, which is found to provide sufficient accuracy. Further increasing the basis size in SIESTA does not affect the quasiparticle energies since the additional resonant orbitals will be removed during the orthonormalization process.

For benzene, we start with 2699 DFT orbitals (15 occupied and 2684 unoccupied), which are sufficient for a convergent calculation within the standard G_0W_0 approach and start to successively reduce the number of unoccupied orbitals and replace them with the SAPOs. We generate the SAPOs with 2701 plane waves and 101 resonant orbitals, which correspond to having energy eigenvalues up to the energy cutoff of 6 Ry above the vacuum level. We construct three sets of SAPOs, corresponding to using 17, 87, and 481 exact DFT orbitals up to -0.09, 0.45, and 1.81 Ry relative to the vacuum level, respectively. To generate the SAPOs, we group the degenerate plane waves into stars, construct a reducible representation for each star, decompose it into irreducible representations, generate basis functions for each irreducible representation, and make symmetric combinations of plane waves. We then orthonormalize the symmetrized plane waves and resonant orbitals from SIESTA calculations, correct the energy eigenvalues, and diagonalize the DFT Hamiltonian according to Eqs. (2), (4), and (5). If the eigenvalues $E_{n\mathbf{k}}$ and $\mathcal{E}_{n\mathbf{k}}$ go above the energy cutoff of 6 Ry, the corresponding SAPOs are thrown away. While generating 2699 DFT orbitals using PARATEC [20] takes 285 CPU core hours on the Cray XE6 supercomputer, constructing 2732 SAPOs only takes 0.7 CPU core hour. It is also important to note that unlike the DFT codes, the generation of SAPOs scales linearly to tens of thousands of processors in the same way as the GW codes [19]. In Fig. 1, we plot the eigenvalues and plane-wave components of the eigenvectors for 87 exact DFT orbitals and 113 SAPOs $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$ of benzene, illustrating that the SAPOs contain the salient features of the exact DFT orbitals.

We now perform G_0W_0 calculations on benzene using the SAPOs. [For benzene, the use of $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$ or $\{\mathcal{E}_{n\mathbf{k}}, \Phi_{n\mathbf{k}}(\mathbf{r})\}$ produces equally accurate results.] To examine separately the effects of the convergence of χ^0 and Σ with different sets of orbitals, we carry out two independent calculations. First, we employ the SAPOs in the calculation of χ^0 and compute the self energy Σ_{COHSEX} in the static Coulomb-hole and screened-exchange (COHSEX) approximation (expressed in a closed form that involves only occupied DFT orbitals) [1]. Second, we compute χ^0 with 2699 exact DFT orbitals and we use
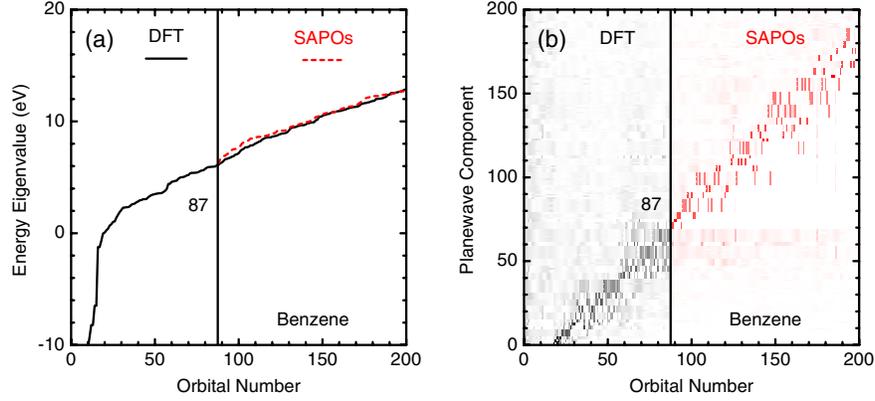
FIG. 1 (color online).   (a) Energy eigenvalues and (b) plane-wave components of the eigenvectors arranged in ascending order by kinetic energy for the electronic orbitals of benzene (C_6H_6). Orbitals 1–87 are obtained from plane-wave DFT calculation. Orbitals 88–200 are the SAPOs $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$ (C + R/E using the notation of Fig. 2). The zero of the energy scale in (a) is aligned with the vacuum level.

the SAPOs for calculating Σ within the generalized plasmon-pole (GPP) model [2]. The resulting Σ_{COHSEX} and Σ for the HOMO of benzene are shown in Fig. 2. For comparison, Σ_{COHSEX} and Σ computed with only DFT orbitals (without the SAPOs), with DFT and continuum orbitals (without the resonant orbitals), and with DFT and resonant orbitals (without the continuum orbitals) are also shown in Fig. 2. From examining Fig. 2, we conclude that both the continuum and resonant orbitals are equally essential to the self energy in molecular systems. The continuum orbitals are accurately approximated by plane waves and the resonant orbitals are easily obtained from a localized basis DFT calculation, but not the other way around. As one can see from Fig. 2, the errors in both Σ_{COHSEX} and Σ computed with only 17 DFT orbitals complemented with the SAPOs converge quickly to within 50 meV of the final answer. We further perform G_0W_0

calculations of the HOMO and lowest unoccupied molecular orbital (LUMO) of benzene employing the three sets of increasing number of SAPOs, $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$, in computing both χ^0 and Σ. The results are summarized in Table I. Again, the errors do not exceed 50 meV from the converged G_0W_0 results even if only 2 unoccupied DFT orbitals are used.

We have tested our method on other molecular and extended systems. For a calculation of buckminsterfullerene (C_{60}), we employ the Perdew-Burke-Ernzerhof exchange-correlation functional [30] and we set $E_\psi = 51$ Ry and $E_\epsilon = 6$ Ry. The size of the unit cell is $38.8 \times 38.8 \times 38.8 \ a_0$. We carry out G_0W_0 calculations with 5490 DFT orbitals (120 occupied and 5370 unoccupied) and with 60 unoccupied DFT orbitals complemented with 5319 SAPOs up to the energy cutoff of 3 Ry above the vacuum level. The generation of DFT orbitals and SAPOs
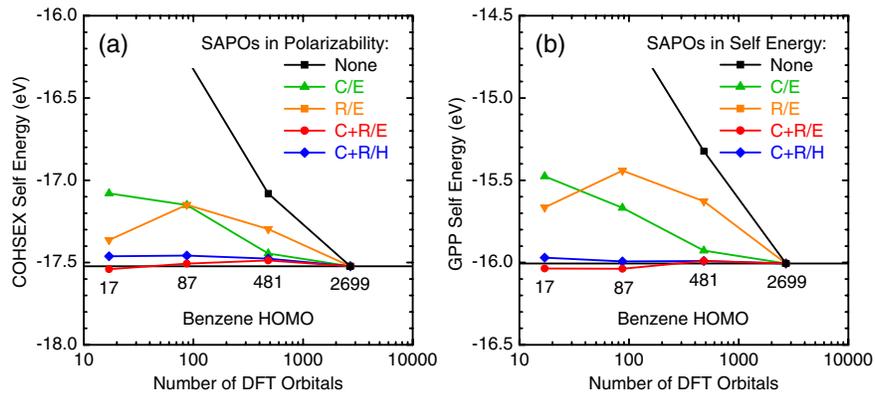

FIG. 2 (color online).   Self energy (a) in the static COHSEX approximation and (b) within the GPP model for the HOMO of benzene (C_6H_6). The sums over orbitals in (a) irreducible polarizability and (b) self energy are computed using 17, 87, 481, and 2699 exact DFT orbitals complemented with the SAPOs made of the symmetrized plane waves and localized basis DFT orbitals that represent the continuum (C) and resonant (R) orbitals of benzene, respectively, up to the energy cutoff of 6 Ry above the vacuum level. The C and R orbitals are orthonormalized according to Eq. (2) with either the energy (E) correction of Eq. (4) applied or the DFT Hamiltonian (H) diagonalization of Eq. (5) carried out. The horizontal lines denote the values computed with 2699 exact DFT orbitals.

TABLE I. HOMO and LUMO levels and the band gap of benzene (C_6H_6) and buckminsterfullerene (C_{60}), and the VBM energy, CBM energy, and indirect band gap of crystalline silicon (c-Si) from DFT, G_0W_0 and experiment [25–29]. The G_0W_0 energies are computed with different numbers of unoccupied DFT orbitals complemented with SAPOs $\{E_{n\mathbf{k}}, \Psi_{n\mathbf{k}}(\mathbf{r})\}$ (C + R/E using the notation of Fig. 2) up to 6 Ry above the vacuum level for C_6H_6 and up to 3, 6, and 9 Ry for C_{60}, and with SAPOs C/E up to 20 Ry above the averaged DFT potential for c-Si.

C_6H_6	No. of unocc. orb.		HOMO	LUMO	E_g
	DFT	SAPOs	(eV)	(eV)	(eV)
DFT	$\cdots$	$\cdots$	-6.49	-1.25	5.24
G_0W_0	2684	0	-9.05	1.51	10.56
	2	2732	-9.10	1.49	10.59
	72	2660	-9.08	1.49	10.57
	466	2249	-9.03	1.54	10.57
Expt.	$\cdots$	$\cdots$	-9.24	1.12	10.36
C_{60}	No. of unocc. orb.		HOMO	LUMO	E_g
	DFT	SAPOs	(eV)	(eV)	(eV)
DFT	$\cdots$	$\cdots$	-5.84	-4.19	1.65
G_0W_0	5490	0	-6.76	-2.18	4.58
	60	5319	-6.77	-2.13	4.64
	60	15 029	-7.09	-2.49	4.60
	60	27 387	-7.21	-2.62	4.59
Expt.	$\cdots$	$\cdots$	-7.64	-2.69	4.95
c-Si	No. of unocc. orb.		VBM	CBM	E_g
	DFT	SAPOs	(eV)	(eV)	(eV)
DFT	$\cdots$	$\cdots$	0.00	0.50	0.50
G_0W_0	407	0	-0.89	0.34	1.23
	28	374	-0.84	0.37	1.21
Expt.	$\cdots$	$\cdots$	$\cdots$	$\cdots$	1.17

takes 5680 and 35 CPU core hours, respectively. To test the convergence, we increase the number of SAPOs to 15 029 (up to 6 Ry) and 27 387 (up to 9 Ry). The resulting quasiparticle energies for C_{60} are listed in Table I. For crystalline silicon (c-Si), we use a local density approximation exchange-correlation functional, $8 \times 8 \times 8$ **k** mesh, $E_\psi = 43$ Ry, and $E_\epsilon = 10$ Ry. SAPOs are obtained by the symmetrization of plane waves using a "small symmetry group" for each **k** point. We perform G_0W_0 calculations with 411 DFT orbitals (4 occupied and 407 unoccupied) and with 28 unoccupied DFT orbitals complemented with 374 SAPOs up to the energy cutoff of 20 Ry above the averaged DFT potential. The generation of DFT orbitals and SAPOs takes 43 and 0.06 CPU core hours, respectively. The quasiparticle energies at the valence band maximum (VBM) and the conduction band minimum (CBM) as well as the indirect band gap E_g for c-Si are shown in Table I. For both C_{60} and c-Si, the errors in using SAPOs are again less than 50 meV.

In summary, we introduced and implemented the concept of SAPOs for use in GW calculations. These SAPOs and their energies are constructed from symmetrized plane waves and localized basis DFT orbitals and orthonormalized with respect to the lower energy DFT orbitals and among themselves. The lower energy DFT orbitals can in turn be constructed using plane-wave or localized basis functions. This approach greatly extends the validity of the simple plane-wave substitution method [15,16]. It is aimed for molecular systems where tens of thousands of unoccupied orbitals are required to converge the GW quasiparticle energies. It is also applicable to extended systems with many atoms per unit cell. It opens an efficient route to accurate GW calculations for large complex systems.

[1] L. Hedin and S. Lundqvist, in *Advances in Research and Applications*, edited by F. Seiz, D. Turnbull, and H. Ehrenreich, Solid State Physics Vol. 23 (Academic Press, New York, 1969) pp. 1–181.

[2] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[3] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[4] S. G. Louie, *Contemporary Concepts of Condensed Matter Science: A Standard Model for Ground- and Excited-State Properties* (Elsevier, New York, 2006).

[5] P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt, and M. Scheffler, New J. Phys. **7**, 126 (2005).

[6] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).

[7] M. Jain, J. Deslippe, G. Samsonidze, M. L. Cohen, and S. G. Louie, (unpublished).

[8] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).

[9] P. Umari, G. Stenuit, and S. Baroni, Phys. Rev. B **81**, 115104 (2010).

[10] F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. B **81**, 115105 (2010).

[11] F. Bruneval and X. Gonze, Phys. Rev. B **78**, 085125 (2008).

[12] J. A. Berger, L. Reining, and F. Sottile, Phys. Rev. B **82**, 041103(R) (2010).

[13] M. L. Tiago and J. R. Chelikowsky, Phys. Rev. B **73**, 205334 (2006).

[14] J. Deslippe, G. Samsonidze, M. Jain, M. L. Cohen, and S. G. Louie, [Phys. Rev. B (to be published)].

[15] L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I. D. White, and R. W. Godby, Comput. Phys. Commun. **125**, 105 (2000).

[16] S. Ismail-Beigi and S. G. Louie (private communication).

[17] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53,** R10441 (1996).

[18] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys. Condens. Matter **14,** 2745 (2002).

[19] J. Deslippe, G. Samsonidze, D. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, [Comput. Phys. Commun. (to be published)].

[20] B. G. Pfrommer, J. Demmel, and H. Simon, J. Comput. Phys. **150,** 287 (1999).

[21] N. Troullier and J. L. Martins, Phys. Rev. B **43,** 1993 (1991).

[22] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48,** 1425 (1982).

[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23,** 5048 (1981).

[24] S. Ismail-Beigi, Phys. Rev. B **73,** 233103 (2006).

[25] G. I. Nemeth, H. L. Selzle, and E. Schlag, Chem. Phys. Lett. **215,** 151 (1993).

[26] P. D. Burrow, J. A. Michejda, and K. D. Jordan, J. Chem. Phys. **86,** 9 (1987).

[27] D. L. Lichtenberger, M. E. Rempe, and S. B. Gogosha, Chem. Phys. Lett. **198,** 454 (1992).

[28] X.-B. Wang, C.-F. Ding, and L.-S. Wang, J. Chem. Phys. **110,** 8217 (1999).

[29] W. Bludau, A. Onton, and W. Heinke, J. Appl. Phys. **45,** 1846 (1974).

[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77,** 3865 (1996).