P H Y S I C A L   R E V I E W   L E T T E R S

Quasiparticle Energies and Band Gaps in Graphene Nanoribbons

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We present calculations of the quasiparticle energies and band gaps of graphene nanoribbons (GNRs) carried out using a first-principles many-electron Green's function approach within the *GW* approximation. Because of the quasi-one-dimensional nature of a GNR, electron-electron interaction effects due to the enhanced screened Coulomb interaction and confinement geometry greatly influence the quasiparticle band gap. Compared with previous tight-binding and density functional theory studies, our calculated quasiparticle band gaps show significant self-energy corrections for both armchair and zigzag GNRs, in the range of 0.5–3.0 eV for ribbons of width 2.4–0.4 nm. The quasiparticle band gaps found here suggest that use of GNRs for electronic device components in ambient conditions may be viable.

Graphene, a single atomic layer of graphite, has been successfully produced in experiment [1–3], which has resulted in intensive investigations on graphene-based structures because of fundamental physics interests and promising applications [4–10]. When graphene is etched or patterned along one specific direction, a novel quasi-one-dimensional structure, a strip of graphene of nanometers in width, can be obtained, which is referred to as a graphene nanoribbon (GNR). The GNRs are predicted to exhibit various remarkable properties and may be a potential elementary structure for future carbon-based nanoelectronics [11–14]. In particular, as a fundamental factor in determining transport and optical properties, the electronic band structure of GNRs has been the subject of great interest.

Depending on specific GNRs, previous studies using tight-binding or massless Dirac fermion equation approaches have predicted GNRs to be either metals or semiconductors [15–20], whereas density functional theory (DFT) calculation showed that all zigzag-edged and armchair-edged GNRs have a finite band gap when relaxation of the structure or spin polarization is considered [13,21]. Recent experiments have reported finite band gaps in all the GNRs that have been tested [22,23]. However, it is well established [24] that the Kohn-Sham eigenvalues from DFT calculation are inappropriate to describe the band gaps of semiconductors. The disagreement between the Kohn-Sham band gap and experimental data is worse for nanostructures because of the enhanced electron-electron interaction in those systems. On the other hand, first-principles calculation based on many-body perturbation theory, such as the *GW* approximation [24,25], has been shown to be reliable for obtaining quasiparticle band gaps of nanosized semiconductors [26–29]. Motivated by the importance but the lack of accurate knowledge about quasiparticle band gaps of the GNRs and by the successes of the *GW* approximation for nano-

size semiconductors, we carry out a first-principles calculation using the *GW* approximation to determine the quasiparticle energy spectrum and the band gaps of the GNRs.

We consider two common types of GNRs. Their structures are shown in Fig. 1. The left one, called armchair GNR (AGNR), has armchair-shaped edges; the right one, called zigzag GNR (ZGNR), has zigzag-shaped edges. The dangling σ bonds at the edges are passivated by hydrogen atoms. The structures of the GNRs studied here are fully relaxed according to the forces and stress on the atoms using local (spin) density approximation [L(S)DA]. Following conventional notation, a GNR is specified by the number of dimer lines or zigzag chains along the ribbon forming the width, for the AGNR and ZGNR, respectively, as explained in Fig. 1. For example, the structure of Fig. 1(a) is referred as a 11-AGNR and the structure in Fig. 1(b) as a 6-ZGNR. In addition, when referring to the width of a GNR here, we define the width without including the hydrogen atoms at the edge, as shown in Fig. 1.
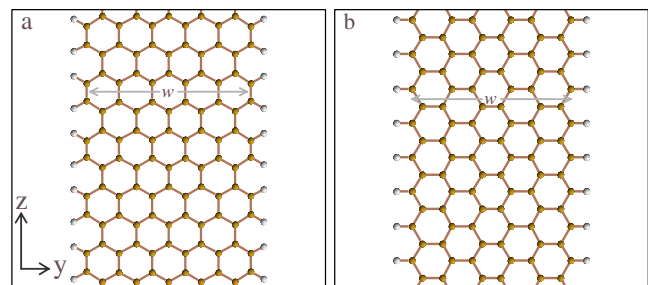

FIG. 1 (color online). (a) A ball-stick model for an 11-AGNR which has 11 C-C dimer lines making up its width w. Hydrogen atoms (white balls) are used to passivate the edge σ-dangling bonds. x, y, and z are the Cartesian coordinates, and the x axis is out of plane. (b) A ball-stick model for a 6-ZGNR which has 6 zigzag chains along the z direction.

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Recently, several experiments related to the quasiparticle band gap in GNRs have been reported [22,23]. They have not only proven the existence of finite band gap in GNRs but also shown a larger gap when the width of the GNR decreases. Within a range of width of GNRs of 15 to 90 nm, a $E_g \propto 1/w$ relation is observed. This finding agrees qualitatively with our *GW* results. However, the experimental data are for the wider GNRs where the widths are far from the range of widths of our calculated GNRs (0.4–2.4 nm). In addition, all the GNRs in the experimental case are etched by the oxygen plasma, which could be different from our hydrogen-passivated GNRs. Therefore, it is difficult to compare our *GW* results with current experimental data directly. On the other hand, considering that the origin of the enhancement of the self-energy correction in GNRs is the quasi-one-dimensional geometry and weakened screening, we expect that other passivating atoms or molecules do not change the physics here significantly. With advances in experimental techniques, it is very possible that smaller-sized and hydrogen-passivated GNRs will soon be fabricated. A comparison between our first-principles results and experimental data can then be made.

In conclusion, we have performed a first-principles Green's function calculation within the *GW* approximation to obtain the quasiparticle band gaps in GNRs. Because of the enhanced electron-electron interaction in these quasi-one-dimensional systems, a significant self-energy correction is found for both armchair and zigzag GNRs. The quasiparticle energy of states near the band gap in ZGNRs is found to be wave vector sensitive, and this gives rise to a larger band width and smaller effective mass for carriers in ZGNRs. The calculated quasiparticle band gaps are within the most interesting range (1–3 eV for 2–1 nm GNRs) and give promise for applications of GNRs in nanoelectronics.

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Self-interaction in Green's-function theory of the hydrogen atom

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Atomic hydrogen provides a unique test case for computational electronic structure methods, since its electronic excitation energies are known analytically. With only one electron, hydrogen contains no electronic correlation and is therefore particularly susceptible to spurious self-interaction errors introduced by certain computational methods. In this paper we focus on many-body perturbation theory (MBPT) in Hedin's *GW* approximation. While the Hartree-Fock and the exact MBPT self-energy are free of self-interaction, the correlation part of the *GW* self-energy does not have this property. Here we use atomic hydrogen as a benchmark system for *GW* and show that the self-interaction part of the *GW* self-energy, while nonzero, is small. The effect of calculating the *GW* self-energy from exact wave functions and eigenvalues, as distinct from those from the local-density approximation, is also illuminating.

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I. INTRODUCTION

Ab initio many-body quantum mechanical calculations are crucially important to our understanding of the behavior of atomic, molecular, and condensed matter systems. It is well-known that predicting the behavior of these systems requires the description of electronic correlation. While density-functional theory (DFT) in the local-density approximation (LDA) does this with startling success in many cases, it does so at the expense of a nonphysical electron self-interaction. For delocalized electron systems this self-interaction becomes negligible, but in atomic or strongly localized electronic systems it plays an important role. If one is interested in the calculation of quasiparticle excitation spectra, many-body perturbation theory (MBPT) is formally a correct way to proceed. For solids, MBPT in Hedin's *GW* approximation [1] has become the method of choice, but it is also increasingly being applied to molecular systems and clusters. The *GW* self-energy can be decomposed into correlation and exchange parts, where the latter is the same as the Fock operator encountered in Hartree-Fock theory and thus self-interaction free. While the exact self-energy must also be free of self-interaction, the correlation part of the *GW* self-energy does not have this property. To investigate the influence of self-interaction in the *GW* approach the hydrogen atom provides an ideal case because the exact solution is known analytically.

Hydrogen in its solid phase has previously been studied within the *GW* approximation by Li *et al.* [2], who analyzed the transition between the high-pressure solid phase and the low density, atomiclike limit. For individual atoms, *GW* electron removal and addition energies (we use the term "quasiparticle" energies by analogy with the solid-state situation)

have been investigated by Shirley and Martin [3], Dahlen *et al.* [4,5], Stan *et al.* [6], and Delaney *et al.* [7], although hydrogen was not considered. These studies have shown that *GW*, in general, gives quasiparticle properties which are much improved over DFT and Hartree-Fock methods, even for atoms.

In this paper we use the hydrogen atom as a benchmark system to quantify the self-interaction error in the *GW* approach. Since the self-energy diagrams *beyond GW*, known as the vertex correction, must by definition correct this self-interaction error, our findings are relevant for research into vertex functions for the many-electron problem.

Attention has recently focused on the prospects for improving the usual non-self-consistent *GW* calculations by choosing an initial Green's function, G_0, that is physically more reasonable than the LDA (e.g., [2,8,9]). We explore this here by determining the sensitivity of the self-interaction error to the use of the exact hydrogenic orbitals and energies in place of those from the local-density approximation (LDA). We also assess the error introduced into *GW* calculations by employing first-order perturbation theory in solving the quasiparticle equation (as opposed to the full numerical solution), and we analyze the quasiparticle wave functions that emerge from a full solution.

II. HARTREE-FOCK VERSUS DFT-LDA

In many-body perturbation theory the quasiparticle excitation energies $\epsilon_{i\sigma}$ and wave functions $\psi_{i\sigma}$ are the solutions of the quasiparticle equation

$$H_0(\mathbf{r})\psi_{i\sigma}(\mathbf{r}) + \sum_{\sigma'} \int d\mathbf{r}' M_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\epsilon_{i\sigma}^{\mathrm{qp}})\psi_{i\sigma'}(\mathbf{r}') = \epsilon_{i\sigma}^{\mathrm{qp}}\psi_{i\sigma}(\mathbf{r}),$$

(1)

where, in Hartree atomic units, $H_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r})$ and $v_{ext}(\mathbf{r})$ is the external potential. It is customary to divide the

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the correct physics in this extreme system (owing to the large self-interaction present in the LDA calculation itself, as reflected in the large error in the LDA Kohn-Sham eigenvalue) that it forms a very unsuitable starting point for *GW*. However, a physically reasonable starting point reduces the *GW* self-interaction error to a small size.

Since Σ_c gives a nonvanishing contribution to the hydrogen 1*s* state, even if the analytic solution is used as a starting point, the quasiparticle wave function will differ from the exact one. Figure 1 shows that the *GW* correlation gives rise to a slight delocalization of the quasiparticle wave function in this case. This relaxation, however, now makes the quasiparticle wave function an eigenfunction of the quasiparticle Hamiltonian. In the LDA the self-interaction error is much more pronounced and the wave function becomes significantly more delocalized. The *GW* self-energy corrects this to a small extent (as reflected in the quasiparticle wave function), but the remaining discrepancy reiterates the unsuitability of the LDA as a starting point for *GW* in this self-interaction-dominated atom.

For an analysis of the contributions to the self-energy we turn to the perturbative solution of the quasiparticle equation using Eq. (17), shown in Table II. When the exact Kohn-Sham wave function and eigenvalues are used, as in the Hartree-Fock case the exchange part of the self-energy is seen to cancel the self-interaction contribution from the Hartree potential exactly. The correlation part, on the other hand, is not zero, but amounts to a self-polarization of 0.25 eV. When the LDA is used as the starting point the influence of the LDA wave function on the exchange operator becomes apparent and it reduces from −17.00 eV in the exact case to −15.38 eV. This corrects the highly overestimated LDA eigenvalue for the 1*s* state of −6.36 eV (see Table I) to −13.49 eV. However, in this case the contribution from the correlation part of the *GW* self-energy is even larger than when starting from the exact case and increases the quasiparticle energy to −12.93 eV.

TABLE II. Quasiparticle energies (eV) for the 1*s* state of hydrogen obtained by solving Eq. (17). The contributions from the exchange $\langle \Sigma_x \rangle$ and correlation $\langle \Sigma_c \rangle$ part of the self-energy are compared to that of the exchange-correlation potential $\langle v_{xc} \rangle$ for the LDA and the exact case ($v_{xc} = -v_H$) as a starting point. Exact value for ϵ_{1s} is −13.61 eV.

Kohn-Sham G_0	ϵ_{1s}^{GW}	$\langle \Sigma_x \rangle$	$\langle v_{xc} \rangle$	$\langle \Sigma_c \rangle$
LDA	−12.93	−15.38	−8.25	0.56
Exact	−13.35	−17.00	−17.00	0.25

VI. CONCLUSION

We have performed spin-resolved benchmark calculations for the *GW* formalism using the analytically known solutions of the hydrogen atom as a reference, making the self-interaction error introduced by the correlation part of the *GW* self-energy directly assessable. When the exact Kohn-Sham Green's function is used as the input to *GW*, the self-interaction error is small (0.21 eV, 1/30 the size of that in the LDA), but not negligible. If the LDA Kohn-Sham Green's function is used, as done in many *GW* calculations for more complex systems, a larger self-interaction error remains, inherited from the LDA starting point.

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Exact-exchange-based quasiparticle energy calculations for the band gap, effective masses, and deformation potentials of ScN

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The band gaps, longitudinal and transverse effective masses, and deformation potentials of ScN in the rock-salt structure have been calculated employing G_0W_0-quasiparticle calculations using exact-exchange Kohn-Sham density-functional theory one-particle wave functions and energies as input. Our quasiparticle gaps support recent experimental observations that ScN has a much lower indirect band gap than previously thought. The results are analyzed in terms of the influence of different approximations for exchange and correlation taken in the computational approach on the electronic structure of ScN.

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I. INTRODUCTION

Scandium nitride (ScN) is emerging as a versatile material for promising technological applications. As part of the transition-metal nitride family it initially generated interest for potential applications as wear-resistant and optical coatings due to its mechanical strength, high melting point of 2600 °C,[1] and high hardness (H=21 GPa) with respect to load deformations.[2] ScN crystallizes in the rock-salt phase with a lattice parameter of 4.50 Å.[3] The octahedral bonding arrangement provides a much more favorable environment for the incorporation of transition-metal atoms like Mn or Cr than the tetrahedrally coordinated III-V semiconductors, which have up until now been popular candidates for spintronic materials. Successful incorporation of Mn into ScN has been demonstrated[4] and *ab initio* calculations predict Mn-doped ScN to be a dilute ferromagnetic semiconductor.[5] Moreover, ScN has a lattice mismatch of less than 2% to cubic gallium nitride (GaN). This makes ScN structurally compatible with the group-IIIA nitrides[6–13]—an important technological material class, in particular, for applications in optoelectronic devices. Alloying ScN with GaN (Refs. 9–12) might provide a viable alternative to InGaN alloys for use in light-emitting devices or solar cells. In addition, multifunctional devices are conceivable if the strong electromechanical response predicted for hexagonal ScN (Ref. 14) can be utilized.

The electronic band structure of ScN—a key quantity for the design of optoelectronic devices—has been difficult to access both experimentally and theoretically. Early experiments were hampered by various complications in growing films with well-defined crystalline orientation, stoichiometry, low background carrier concentration, and surface roughness. For a detailed discussion we refer to, e.g., Ref. 15. Recent advances in growth techniques have led to a systematic improvement of the material's quality.[16] Employing optical spectroscopy and photoemission, Gall *et al.*[15] concluded that ScN is a semiconductor with an indirect $\Gamma-X$ band gap ($E_g^{\Gamma-X}$) of 1.3±0.3 eV. The sizable error bar of 0.3 eV has been mainly attributed to the large background carrier concentration of $\sim 5 \times 10^{20}$ cm^{-3} causing an apparent increase of the band gap due to the Burnstein-Moss shift.[17] Reducing the electron carrier concentration to 4.8×10^{18} cm^{-3} and combining tunneling spectroscopy and optical-absorption measurements, Al-Brithen *et al.*[18] were able to reduce the error bar and found a value for $E_g^{\Gamma-X}$ of 0.9±0.1 eV.

Early Kohn-Sham density-functional theory (KS-DFT) calculations employing the local-density (LDA) or $X\alpha$ approximations predicted ScN to be a semimetal with a small negative band gap between −0.01 and −0.21 eV.[19–21] In order to overcome the well-known underestimation of the LDA band gap, more advanced exact-exchange [OEPx(cLDA)] (Ref. 15) and screened-exchange[22] calculations have been performed, and showed that ScN is a semiconductor with an indirect Γ to X band gap, in accord with experimental evidence.[15,18] However, the calculated band gap of 1.60 eV found in both studies is significantly larger than the most recent experimental value of 0.9±0.1 eV.[18]

In order to shed light on this discrepancy we have performed quasiparticle energy calculations in Hedin's GW approximation,[23] which is a well-established technique to calculate accurate band-structure energies and currently the choice for computing quasiparticle band structures of solids.[24–26] The quasiparticle calculations predict ScN in the rock-salt phase to have an indirect band gap between the Γ and X point of 0.99±0.15 eV, strongly supporting recent experimental findings. In addition, we have also determined the direct band gaps and other electronic structure parameters relevant for device simulations: the volume deformation potentials of the main band gaps and the longitudinal and transverse effective masses of the conduction band at the X point. The effective mass has previously been calculated at the level of the LDA,[27] but to the best of our knowledge, only one experimental study has reported a conduction-band ef-

IV. CONCLUSIONS

Pseudopotential G_0W_0 calculations based on Kohn-Sham density-functional theory calculations in both the LDA and OEPx(cLDA) have been performed for the electronic structure of ScN in the thermodynamically stable rock-salt phase. To analyze the effects of exchange and correlation the atomic and electronic structures have been studied within DFT for several levels of approximations for the exchange-correlation functional [LDA, GGA and OEPx(cLDA)]. In agreement with previous calculations for ScN, our LDA [OEPx(cLDA)] band gaps are underestimated (overestimated) by about 100%. Despite this large difference, OEPx(cLDA)-G_0W_0 and LDA-G_0W_0 calculations for the quasiparticle band structure agree to within 0.3 eV. Our quasiparticle gap of 0.99 ± 0.15 eV supports the recent observation that ScN has a much lower indirect band gap than previously thought. The main advantage of the OEPx(cLDA)-G_0W_0 approach lies in the fact that it facilitates a direct calculation of the electronic structure of ScN at the experimental equilibrium volume, whereas for the LDA-G_0W_0 calculation an indirect approach has to be taken due to the negative LDA band gap.

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Density dependence of the momentum distributions in liquid *para*-hydrogen

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Momentum distributions of liquid *para*-hydrogen were determined by means of inelastic neutron scattering under applied pressures ranging from 1 to 80 bars, at $T=16.5$ K. The data processing procedure involves the parametrization of the dynamic structure factor and yields a set of momentum distributions as functions of the density. The results depict significant pressure dependences for all single-particle quantities such as the momentum distributions and average kinetic energies as well as for the final-state effects. The obtained results enable us to quantify the departure of the momentum distributions from classical Maxwell-Gauss shape. Such observations are then rationalized with the help of calculations that were carried out in terms of the correlated density matrix formalism.

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I. INTRODUCTION

Neutron scattering measurements at large momentum transfers have proven to be the most adequate tool for the determination of single-particle properties of solids and fluids exhibiting noticeable quantum dynamics features.[1] The sought quantities are the momentum distributions $n(k)$ as well as the atomic kinetic energies. The former quantities are defined as the thermal average of the number of particles having momenta with wave number k at a given particle density and temperature. For condensed bodies showing strong quantum effects one expects to retrieve from experiment direct indications of quantum dynamics such as translational kinetic energies $\langle E_K \rangle_T$ well in excess of those estimated on the grounds of classical statistical mechanics—that is, $\langle E_K^{cl} \rangle_T = 3k_B T/2$—as well as momentum distributions showing noticeable deviations from the Gaussian shape as predicted on the grounds of the Maxwell-Boltzmann distribution. During the last decade, such methods have provided direct quantitative information on the bounds for the Bose condensate fraction for liquid ^{4}He (Ref. 2) as well as estimates for kinetic energies calculated from the Gaussian component of $n(k)$ at 2.5 K. The latter amounts to 15.7 K, versus that of $\langle E_K^{cl} \rangle = 3.75$ K, and drops to about 14 K upon crossing the superfluid transition.

While the case of condensed heliums is now well understood, other fluids such as the condensed hydrogens, which exhibit strong quantum features due to their low molecular masses and low temperatures characteristic of their liquid ranges, still are in need of a fully quantitative account of the importance of such quantum effects.

Previous results on liquid and solid hydrogen and deuterium[3–7] have mostly dealt with the estimation of translational kinetic energies or rough estimates of the momentum distribution using large incident energies. This ensures that the incoherent limit is attained, thus minimizing the effects brought forward by the interaction of the particle once struck by the incoming neutron with the rest of the system, usually referred to as final-state effects (FSE's). In contrast, such studies are affected by the inherently low resolution achievable using incident energies of the order of a few eV as well as significantly excite the intramolecular vibrations, an effect that introduces some additional complications for accurately modeling of the cross sections.[4] In fact, for incident neutron energies above the molecular vibrational threshold $\hbar\omega_\nu \approx 516$ meV, one expects scattering due to individual atoms rather than from the molecule as a whole and therefore two separate contributions to the kinetic energy need to be considered. The spectrum, usually transformed into a form usually referred to as a neutron Compton profile, is now a convolution of vibrational and translational components.[4] On the other hand, for incident energies that are large compared to those characterizing the collective dynamics but below the vibrational threshold,[8–10] the spectrum for a molecular material such as *para*-hydrogen which has a spherically symmetric rotational ground state[12] will be comparable to that of a monatomic system which recoils with a total mass equal to the molecular mass.

The study here reported on concerns the density dependence of the single-particle properties of (mostly) liquid *para*-hydrogen studied at moderate-to-large momentum transfers under conditions that avoid the excitation of the first vibrational level. The present effort follows others where the spectrum of the collective excitations of both molecular hydrogen and deuterium have been described in detail[9–11] with emphasis put on the characterization of the transition between collective and single-particle regimes.

The interest in the present exercise is twofold. The first concerns some recent findings pointing towards anomalies in the density dependence of some of the dynamical properties of liquid *para*-hydrogen.[13] Second and from a more fundamental standpoint, it concerns some recent predictions made on the grounds of correlated density matrix (CDM) theory.[14]

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Quasiparticle energy bands of NiO in the *GW* approximation

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We present a first-principles study of the quasiparticle excitations spectrum of NiO. The calculations are performed using the spin-polarized *GW* approximation in a plane-wave basis set with *ab initio* pseudopotentials. We find a feature in the band structure which can explain both an absorption edge of 3.1 eV in optical measurements and an energy gap of 4.3 eV found in XPS/BIS measurements. The calculated quasiparticle density of states shows that the oxygen 2*p* peaks overlap with the satellite structure at ~8 eV below the Fermi level. Finally, we discuss the difference between this work and two previous quasiparticle energy calculations.

Since the early days of band theory, NiO has been one of the most intensively studied transition metal mono-oxides. In a purely ionic picture of NiO, the Ni ions have a partially filled 3*d* shell which should result in a metallic behavior according to conventional band theory. However, experimentally, NiO is found to be an insulator. The value of ~4 eV is most often cited for the fundamental gap,[1,2] but this value needs to be taken with caution. Indeed, the measured optical absorption coefficient of NiO shows an onset of absorption at 3.1 eV and reaches its maximum at 4.3 eV.[3] Very similar results are also obtained from UV-isochromat on oxidized nickel[4] and electron energy-loss spectroscopy.[5]

Understanding the electronic structure of NiO is a topic of great interest both for experimentalists and theorists, which has given rise to some controversy in the literature. For a long time, NiO was considered as a prototype Mott insulator in which the insulating gap is caused by the on-site Coulomb energy U.[6] However, this view was challenged based on photoemission and inverse photoemission measurements and model calculations.[1,2] It was proposed that NiO should be categorized as a charge-transfer insulator, the gap resulting predominantly from a $d^8 + d^8 \rightarrow d^8L + d^9$ intercluster transition (L denotes a ligand 2*p* hole). This latter explanation has gained a wide acceptance since it is able to explain most of the experimental data. However, Hüfner *et al.*[7] recently reinvestigated the experiment and concluded that it could not be excluded that the optical gap in pure NiO corresponds to the transition from Ni 3*d* bands into an empty 3*d* band.

Standard band-structure calculations in the local spin density approximation[8] (LSDA) produce a gap (0.3 eV) which is one order of magnitude smaller than the measured band gap. The calculated magnetic moment is also much smaller than the experimental data. These are the key reasons to question the validity of mean field one-electron band theory to describe the electronic structure of NiO. There have been several attempts to calculate the NiO band structure beyond the LSDA. For localized states (e.g., 3*d* electron states), the generalized gradient approximation (GGA) allows one to take into account more the effects of varying density than the LSDA. Some recent publications[9–12] using Kohn-Sham energy eigenvalues from the GGA, however, gave quite a wide range of band gaps (from 0.5 to 1.2 eV) for NiO. The discrepancy may come from that the angular gradient is not

properly taken into account in some studies and thus a smaller band gap.[10] Other "improved" computational schemes such as the self-interaction corrected density functional theory (DFT) and the model LSDA+U methods have also been applied to transition metal oxides.[13–15] Beyond the methods based on DFT, a Green's function approach using the *GW* approximation has been shown to be quite accurate in calculating the quasiparticle excitations for a wide variety of semiconductors and insulators.[16,17] Lately, a few quasiparticle band structure calculations have also been conducted for NiO.[18–20] However, despite all these studies rely on LSDA calculations as a starting guess for constructing the electron self-energy operator, the energy gaps obtained do not agree with each other. This is due to the underlying different approximations, self-consistency, and assumptions used.

Recently, we have demonstrated in the framework of the study of the metal-insulator transition in solid hydrogen that the band gaps calculated by LSDA+*GW* and GGA+*GW* methods differ.[21] Moreover, it was found that the GGA +*GW* method is in better agreement with VQMC and experiment. The difference was attributed to the LSDA and GGA energy spectrum, the GGA eigenfunctions and eigenvalues being closer to the quasiparticle calculation results. In particular, for localized 3*d* electron states, GGA takes into account the moderately varying density rather than LSDA which is based on results of the homogeneous electron gas. Hence, using the GGA as a starting point for the *GW* method seems the obvious next step towards the understanding of the NiO electronic structure. This is the aim of the present study.

In this Brief Report, we present *ab initio* quasiparticle (QP) calculations of NiO in the *GW* approximation. The quasiparticle band structure is compared to the detailed angle-resolved photoemission spectra (ARPES) data. With this quasiparticle band structure, it is possible to explain both the optical absorption edge seen in optical measurements and the fundamental gap found in photoemission (XPS) and inverse photoemission (BIS) experiments. The quasiparticle density of states (DOS) is obtained using the quasiparticle energies and is in good agreement with experiment. Finally, we discuss the difference between this work and previous quasiparticle energy calculations.

In brief, we performed spin-polarized *GW* calculations for NiO using a plane-wave basis. Within this formalism, we have calculated the quasiparticle band structure and found interesting features. The agreement between calculated and experimental (ARPES) band structure is improved compared with LDA or GGA results. In addition to a 4.2 eV band gap which separates the empty *d* states from the valence bands, new features found in the quasiparticle band structure include a lowest *s*-like conduction band at the Γ point which forms an energy gap of 2.9 eV. This picture is consistent with the observed onset of optical absorption at 3.1 eV and a fundamental band gap at 4.3 eV found in BIS-XPS. We also found oxygen 2*p* states at $\sim$8 eV below the Fermi level where satellite structures are observed.

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Systematic study of electron localization in an amorphous semiconductor

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We investigate the electronic structure of gap and band tail states in amorphous silicon. Starting with two 216-atom models of amorphous silicon with defect concentration close to the experiments, we systematically study the dependence of electron localization on basis set, density functional, and spin polarization using the first-principles density-functional code SIESTA. We briefly compare three different schemes for characterizing localization: information entropy, inverse participation ratio, and spatial variance. Our results show that to accurately describe defected structures within self-consistent density-functional theory, a rich basis set is necessary. Our study revealed that the localization of the wave function associated with the defect states decreases with larger basis sets and there is some enhancement of localization from generalized gradient approximation relative to local-density approximation. Spin localization results obtained via local spin-density approximation (LSDA) calculations are in reasonable agreement with experiment and with previous LSDA calculations on *a*-Si:H models.

I. INTRODUCTION

Amorphous semiconductors represent a large and important area in materials science, with interest both from the technological and fundamental point of view. Coordination defects in *a*-Si are of key importance to bulk and transport properties. Understanding the nature of defects in *a*-Si can help unlock the mystery behind phenomena such as the Staebler-Wronski effect[1] and help establish the link between localization of defect states and large electron-phonon coupling. Early theoretical work on defect states in *a*-Si and *a*-Si:H was based on tight-binding methods.[2–7] For example, Biswas *et al.*[2] and Fedders and Carlsson[4] investigated the electronic structure of dangling and floating bonds in *a*-Si. They showed that gap defect states associated with dangling bonds are strongly localized on the central atom of the dangling bond.[2] More recently, density-functional calculations of dangling-bond states using the local-density approximation[8] (LDA) have been performed by Fedders and Drabold.[9] They reported a wave-function localization of 10–15 % on the central atom in supercell models with one defect and far less on supercell models with many defects due to defect band formation. This finding was at variance with electron-spin resonance (ESR) experiments, which showed that over 50% of spin density of the gap state is located on the central atom of the dangling bond.[10,11] However, recent calculations by Fedders *et al.*,[12] using the local spin-density approximation (LSDA), have shown that a large spin localization of a defect state does not necessarily imply the existence of a corresponding wave-function localization.

Density-functional theory[13] (DFT) has enjoyed enormous success in describing the ground-state properties and defects for a wide range of materials, and in particular, *a*-Si. Nonetheless, the one-particle Kohn-Sham energies in the theory have no formal justification as quasiparticle energies. However from an empirical point of view, Hybertsen and Louie have shown, using GW calculations,[14] that for states close to the fundamental band edges of bulk semiconductors and in

particular Si, there is a 99.9% overlap of the quasiparticle wave function with the corresponding Kohn-Sham orbital (GW calculations provide post Hartree self-energy corrections to DFT/LDA). This provides some rationale for interpreting the Kohn-Sham orbitals as quasiparticle states.

Within the density-functional framework, there is a general problem for the accurate representation of localized midgap and band tail states in amorphous semiconductors. The reliability of density-functionals to correctly reveal the localized behavior of electronic states with respect to its wave function and spin is very important. In particular, the generalized gradient approximation (GGA) and LSDA results for electron localization are sometimes quite different. For example, recent density functional and GW studies of the metal-insulator transition of bcc hydrogen showed that eigenfunctions obtained GGA are more localized[15,16] and closer to quasiparticle energies and states than LSDA. Also, it was observed that GGA band gap was systematically larger than LSDA gap.[15]

In this paper, we systematically examine the localization of band tail and gap states and its dependence on basis sets, density functionals, and spin polarization for three defected models: two 216-atom supercell models of amorphous Si and a 218-atom supercell model of crystalline Si:H with a vacancy. The crystalline model will serve as a benchmark to compare the nature of a dangling-bond defect state in an amorphous environment with that of the crystalline phase. We compare the localization of gap and tail states within the LDA, LSDA, and GGA for frozen lattices (unrelaxed samples) as well as for samples fully relaxed for a given Hamiltonian. Our motivation for performing the frozen lattice calculation is to systematically investigate the sole effect of different basis sets and density functionals on the localization of states for a fixed configuration. We study the relaxation effects to see the dependence of the local geometry of the defect sites on the different basis orbitals and density functionals and the behavior of localized defect states in a relaxed environment compared to the frozen one. We com-

IV. CONCLUSION

We have performed a first-principles electronic structure calculation on three Si supercells: two 216-atom supercells of amorphous silicon with two dangling bonds and one 218-atom supercell of hydrogenated crystalline silicon with a void. Depending on the initial distance between the dangling bonds, the two *a*-Si models have been classified as CLOSE and FAR. We examined the nature of localized band tail and gap states within the LDA and GGA using both minimal SZ basis and more complete DZP basis with particular attention paid to relaxation effects. Spin localization and wave-function localization for dangling-bond defect states has also been studied. We computed the wave-function localization as the spread of the wave function in real space and via other measures that utilize the Mulliken charges.

For the frozen lattice calculations, we find that the localization of wave functions associated with defect states decreases with larger basis sets and has enhancement of localization using GGA compared to LDA for all the models. The reduction in charges at the atomic sites for a larger basis set can be attributed to the hybridization between the atomic orbitals, providing the electronic charges more degrees of freedom to redistribute themselves. This is reflected in a smaller distance between the defect states and the band-gap edges, which also favors delocalization. Unpaired spin LSDA calculations performed on frozen lattices showed that the degrees of spin and wave-function localization are different. In particular, degree of spin localization at a dangling-bond site is far greater than the degree of wave-function localization. The difference between the localization of a defect state in a fully relaxed and frozen systems is nontrivial, especially in the minimal basis calculations. In particular, there was a considerable reduction in localization (as measured using the Mulliken charge) for the relaxed systems compared to the frozen lattices. We also conclude that a large basis set (DZP in this case) is necessary for an accurate description of both the geometry and localized states associated with defect sites.

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Static structure factor of liquid parahydrogen

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The single-differential neutron-scattering cross section of liquid parahydrogen has been measured at 15.2 K and 2 bars of applied pressure by means of low-energy neutron diffraction. Our experimental conditions enable the direct observation of the peak of the liquid structure factor and therefore largely improve the signal-to-noise ratio with respect to measurements carried out using higher-energy neutron diffraction. This avoids the need of performing corrections of approximate nature to the measured cross section that is dominated by molecular rotational components if measured by conventional neutron diffraction.

I. INTRODUCTION

Our interest in the basic microscopic properties of condensed molecular hydrogen (solid, liquid, or highly compressed fluid) stems from widely different origins that stretch from astrophysics (it is known to be one of the dominant constituents of the giant planets[1]) to basic condensed-matter physics where efforts to cross the insulator-to-metal transition resulting in the production of metallic hydrogen continue apace.[2]

In contrast, the basic quantity $g(r)$ (the radial pair distribution) that is related to many thermodynamic functions for a liquid has not yet been accurately determined for liquid para-H_2. While neutron diffraction is the prime experimental technique for the purpose just referred to, there exist a number of serious difficulties that hinder a measurement of the static structure factor $S(Q)$ on an absolute scale. Such difficulties arise from the light masses of its constituent particles and the relatively low temperatures where the liquid exists under its saturated vapor pressure. This makes quantum effects prominent, and its first manifestation is the appearance of a discrete spectrum of transitions between molecular rotational levels. The quantum nature of such motions imposes some symmetry constraints on the total molecular wave function. This means that the rotational states and the nuclear-spin states of the two protons forming the H_2 molecule will not be independent. Coupling of nuclear-spin states ($I=0$ for a molecule having antiparallel proton spins and $I=1$ for parallel spin states) leads to two distinguishable species, para-H_2 and ortho-H_2, respectively.

In addition, it is known from the early days of neutron scattering[3] that the cross section for liquid hydrogen is extremely sensitive to the incident neutron energy E_0 and, in fact, for $E_0>80$ meV there is basically no distinction between the total scattering cross sections of normal and pure para-H_2 since the scattering becomes dominated by molecular rotational para→ortho transitions. The latter are known to

follow molecular form factors that exhibit a wave-vector dependence[4] rather different from that corresponding to the liquid-structure factor $S(Q)$. The strength of such rotational contribution nearly doubles that comprising the liquid static structure and consequently it dominates the $d\sigma/d\Omega$ accessible to conventional diffraction using hot or epithermal neutrons.

A previous attempt to derive an estimate for $S(Q)$ (Ref. 5) from an inelastic-scattering experiment yielded a value for its height well in excess of that predicted from path-integral-centroid-molecular-dynamics (PICMD) simulations.[6] Here we report on an experiment conducted using a cold neutron diffractometer that allows us to explore $d\sigma/d\Omega$ under conditions where most of the scattering arises from liquid structure effects rather than single-particle molecular rotations. Contrary to our previous measurement which was not designed for structure determination, the present experiment allows us to measure $d\sigma/d\Omega$ on absolute units from where an estimate of $S(Q)$ for Q-values comprising the liquid diffraction peak is derived. On the other hand, under the experimental conditions we are forced to use, a large part of the scattering is inelastic, thus making the usual approximations employed to analyze experimental data to break down. This is a consequence of the closeness of the incident neutron energy to that required to excite a longitudinal phonon. In consequence, extreme care has been taken to apply nonstandard inelasticity corrections that are described in detail in the coming sections.

II. EXPERIMENT

The neutron measurements were performed at D1B spectrometer (ILL, Grenoble) at a temperature of 15.2 K and 2 bars of applied pressure. The sample was obtained from high-purity hydrogen gas transformed to para-H_2 by forcing it to pass through an activated catalyst, in a similar procedure as described in a previous paper.[7] The sample holder was an

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words, $S_{beads}(Q)$ compares well to the quantity obtained from path-integral monte carlo simulations. Experimental determination of such radial distributions requires the static approximation to hold or, in other words, a sampling time short enough so that a true static picture of the liquid structure can be made. Such conditions cannot be matched in neutron work for reasons explained at the beginning, and use of x-ray beams will only provide an estimate for $g(r)$ about one order of magnitude less accurate than neutrons.[19]

On the other hand, one expects $S_{centroids}(Q)$ to match the result measured using low incident energies since its dynamic counterpart $S_{centroids}(Q,\omega)$ was found to be in good agreement with experimental spectra,[5,6] and therefore it

should come as no surprise that the quantity derived by recourse to Eq. (20) in an inelastic-scattering measurement[5] matches the present result shown in Fig. 3.

Finally, the present set of data are at variance with those reported by Zoppi *et al.*[29] which were derived from hot neutron diffraction. As referred to above and already explained in detail,[6] the difference in both measurements cannot explained only be by the rather different conditions employed in both experiments. In fact, the liquid peak becomes barely visible in the single-differential cross section reported in Ref. 29, and therefore the systematic accuracy claimed by Zoppi *et al.*[29] in their estimate of $S(Q)$ which yields a peak height somewhat below 2.0, seems grossly exaggerated.

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Implementation of an all-electron GW approximation based on the projector augmented wave method without plasmon pole approximation: Application to Si, SiC, AlAs, InAs, NaH, and KH

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An implementation of the GW approximation (GWA) based on the all-electron projector-augmented-wave (PAW) method is presented, where the screened Coulomb interaction is computed within the random-phase approximation (RPA) instead of the plasmon-pole model. Two different ways of computing the self-energy are reported. The method is used successfully to determine the quasiparticle energies of six semiconducting or insulating materials: Si, SiC, AlAs, InAs, NaH, and KH. To illustrate the method the real and imaginary part of the frequency-dependent self-energy together with the spectral function of silicon are computed. Finally, the GWA results are compared with other calculations, highlighting that all-electron GWA results can differ markedly from those based on pseudopotential approaches.

I. INTRODUCTION

For many weakly correlated materials, the density-functional theory[1] (DFT) in the local-density approximation (LDA) provides a good description of their ground-state properties. However, DFT is not able to describe correctly their excited states. Thus, for example, the band gaps in the LDA are typically much smaller than the experimental values. Quasiparticle (QP) electronic-structure calculations beyond the DFT are therefore highly desirable.

The GW approximation (GWA) of Hedin,[2,3] which produces a good approximation for the electron's self-energy Σ, enables us to make first-principle QP calculations for realistic materials. Thus the GWA has been successfully applied to the calculation of QP electronic structures of many kinds of materials.[4–7] In particular, recent success has been achieved on predicting the metal-insulator transition of bcc hydrogen,[8] electronic excitations of yttrium trihydride,[9] as well as the QP electronic structure of copper.[10] Unfortunately, most of the GWA implementations are based on the pseudopotential type of approaches together with plasmon-pole (PlP) models.[11–16] The weakness of these types of calculations is that the imaginary part of the self-energy is not accessible, making it impossible to determine spectral functions and hence to interpret photoemission experiments. In addition the PlP approximation is expected not to hold for systems with localized electrons. Moreover, it has been noticed recently[15,17] that GWA implementations based on pseudopotential methods lead to larger and more **k**-dependent shifts than calculations based on all-electron DFT methods, bringing into question the validity of the former approaches.

However, some attempts have been made to go beyond the plasmon-pole approximation.[7,10,17–21] In particular, Aryasetiawan has approximately determined the screening within the RPA using a linear muffin-tin orbital method within the atomic sphere approximation[7] (LMTO-ASA). This method, although fast, approximates the space by atomic centered overlapping spheres, thus completely neglecting the interstitial region, and hence making the reliability of the GW method uncertain. Kotani and van Schilfgaarde based their full-potential LMTO GW calculation[17] on the work of Aryasetiawan by taking into account correctly the interstitial region. Nevertheless, their method is not quite accurate since in their implementation they did not take into account the multiplicity of the same angular momenta for a given principal quantum number in the basis set (like simultaneously using the $3d$ and $4d$ states). Finally, Ku and Eguiluz produced self-consistent and non-self-consistent QP band gaps based on an approximate Luttinger-Ward functional,[18] the non-self-consistent results are much smaller than all existing GW calculations. Since these results are based on a different scheme we have chosen not to discuss their method further. On the other hand, several pseudopotentials have produced GW results without resorting to the plasmon-pole approximation. These methods, although interesting, use pseudowave functions and hence can only determine pseudomatrix elements of operators, making them difficult to justify as quantitative and reliable methods for computing QP properties.

The major purpose of this paper is then to present a different implementation of the GWA method using the all-electron full-potential projector augmented wave method (PAW) *complete* basis set, and without using any PlP model for the determination of the dielectric function. The screening of the Coulomb interaction is thus described in the random-phase approximation (RPA), avoiding further approximations.

The paper is organized as follows. In Sec. II we describe our implementation of the GW approximation. In Sec. III we present our QP calculations for Si, SiC, AlAs, and InAs and also for the alkali hydrides compounds NaH and KH. At the

Since our method can compute the imaginary part of the self-energy, we could then determine the QP lifetimes, a task not possible using the PlP approximation. Further inspection of spectral properties as well as the computation of QP lifetimes will be presented in future work. The method is currently being applied to determine the excitation properties of LiH, and the results will be reported elsewhere.[60] Moreover, the use of symmetry and an efficient implementation makes us confident that we will soon be able to study systems with a large number of atoms per unit cell, like surfaces or polymers. Furthermore, because we use a mixed basis set in our implementation we could study systems with localized "d"

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Pressure-induced simultaneous metal-insulator and structural-phase transitions in LiH: A quasiparticle study

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Abstract. – A pressure-induced simultaneous metal-insulator transition (MIT) and structural-
phase transformation (from the B1 to B2 phase) in lithium hydride with about 1.3% volume
collapse has been predicted by means of the generalized-gradient approximation (GGA) in
conjunction with an all-electron GW approximation method. The local-density approximation
(LDA) wrongly predicts that the MIT occurs before the structural phase transition, whereas
the GGA predicts the correct transition but with a very small band gap of the B1 phase at the
transition. It is also shown that only the use of the GGA together with the zero-point vibration
produces an equilibrium lattice parameter, bulk modulus, and an equation of state that are in
excellent agreement with experiment.

Lithium hydride is probably the simplest compound that exists: a strongly ionic crystal
with four electrons per unit cell and crystallizing in the rocksalt structure, the so-called B1
phase. Despite this simplicity, LiH and its isotopes are attractive for the study of solid-state
properties, *e.g.*, electronic structure, lattice vibration, and defect properties. In addition,
possible technological applications have motivated extensive studies in the past, as reviewed
by Islam [1]. In particular, the metal-insulator transition (MIT) has been studied by several
groups [1–8]. In few alkali hydrides a structural phase transition (PT) from the B1 phase to
the B2 (CsCl structure) phase was determined experimentally [1, 7] and theoretically [8–10]
within the local-density approximation. It has been only recently that LiH was found to
exhibit the same type of PT but at a much higher pressure [9]. Despite this extensive study,
we believe, as will be shown later, that this PT is not well understood. The purpose of this
letter is then to present results improving the current understanding of the electronic structure

and the GGA predicts the simultaneous MIT and structural PT, but unfortunately it shows a continuous decrease of the band gap that almost vanishes at the transition, in agreement with the results of ref. [9]. Thus, a quasiparticle study is required for a good understanding of a combined MIT and structural PT under pressure.

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