Ab Initio Calculations of the Quasiparticle and Absorption Spectra of Clusters: The Sodium Tetramer

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We report the first *ab initio* quasiparticle calculation in a real cluster Na_4 within Hedin's *GW* approximation for the valence electron self-energy. Our approach avoids the summations over empty states, and also eliminates the problem of residual interactions between the periodic images. Self-energy corrections open the local density approximation gap by more than 2 eV; finite-size effects on screening are shown to play an important role. The absorption spectrum calculated by including excitonic effects using our *ab initio* screened interaction gives a good account of the experimental photodepletion data.

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Density-functional theory (DFT) in the local density approximation (LDA) is a widely and successfully used state-of-the-art tool for computation of the ground-state properties of many-electron systems [1]. DFT can be applied to systems as complex as surfaces, defects, and clusters. However, while the ground-state properties can in principle be obtained exactly, many spectroscopic properties are in general not directly accessible in a DFT calculation. Strictly speaking, it is wrong to interpret the eigenvalues of the Kohn-Sham equation as electron addition or removal energies [1], such as those measured in photoemission. Instead, the quasiparticle (QP) energies of the system should be computed [2]. When electron-hole pairs are created, as in photoabsorption measurements, separate account must be taken of the excitonic binding of the electron and hole quasiparticles.

The state-of-the-art approach to calculating QP spectra is Hedin's *GW* approximation [3], in which the nonlocal, energy-dependent electronic self-energy (which plays a similar role to the exchange correlation potential of DFT) is approximated by a convolution of the one-electron Green's function and the dynamically screened Coulomb interaction. Actual computations of QP energies within the *GW* approach can be performed on real physical systems starting with the DFT-LDA results [4–6]. The numerical effort required to perform a full *GW* calculation has restricted its use to relatively simple structures (with a few exceptions, as in Ref. [7]). For more complex systems approximate *GW* schemes have generally been used (e.g., [8]).

Atomic and molecular clusters are one of the fields in which DFT-LDA has been extensively used to determine ground-state structural and electronic properties, especially with the Car-Parrinello method [9]. However, the theoretical understanding of the electronic excitations and optical spectra relies mostly on configuration interaction (CI) calculations [10,11], which, although highly accurate, are limited to systems with a small number of electrons (of the order of 10). *GW* calculations for clusters have been reported only within the simplified jellium-sphere scheme [8]. Moreover, an understanding of the role of excitonic effects in the absorption spectrum of a small cluster is completely lacking. A strong need exists for a numerically flexible, though sophisticated, theoretical approach and for a clear physical picture of the dominant electronic excitations in small clusters.

In this work, we report a first-principles calculation of the quasiparticle energies and absorption spectrum of a nonjellium sodium cluster Na_4 and compare our results with CI calculations [11] and with experiment [12]. We perform a *GW* calculation based on a new computational approach, which allows us to include, for the first time, the effects of the real geometrical structure of a cluster on its quasiparticle energies. Starting from the QP spectrum, we also evaluate within an *ab initio* approach the exciton states, which we show to be crucial for the interpretation of optical absorption.

We first calculate the ground-state electronic properties of the sodium tetramer, using the DFT-LDA pseudopotential-based Car-Parrinello method [13]. The technical details are the same as in Ref. [14]. We use an energy cutoff of 10 Ry and an fcc supercell of edge $a = 36$ a.u. Convergence with respect to both cutoff and cell size has been carefully tested. The Na_4 equilibrium structure turns out to be a planar rhombus, in agreement with the general consensus from calculations of different levels of sophistication [11,15]. Figure 1 shows the low-lying Kohn-Sham orbitals. The dipole-allowed transitions between them are indicated; these are from the highest occupied molecular orbital (HOMO) ($1b_{3u}$) to the $2a_g$, $1b_{1g}$, $3a_g$, and $1b_{2g}$ states, and from the inner occupied state ($1a_g$) to $1b_{2u}$ [the lowest unoccupied molecular orbital (LUMO)] and $1b_{1u}$. The corresponding LDA optical absorption peaks are shown in the inset of Fig. 2,

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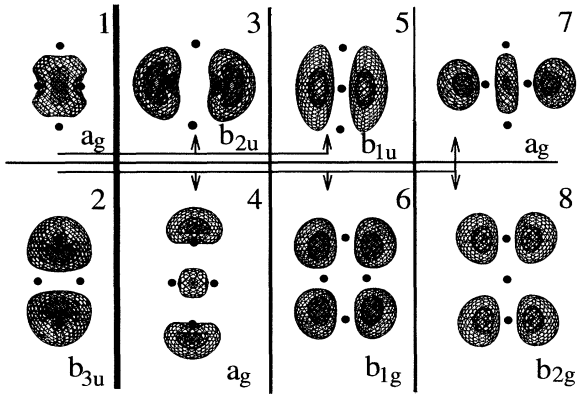

FIG. 1. Shape and symmetry of the lowest Na_4 Kohn-Sham orbitals, numbered by increasing energy. Two surfaces are shown, corresponding to electron densities of about 1×10^{-3} and 2×10^{-3} a.u.$^{-3}$. The cluster symmetry is D_{2h}, and the dipole allowed transitions are indicated by arrows. Only the two lowest states ($1a_g$ and $1b_{3u}$) are occupied.

compared with the experimental absorption spectrum [12]. Agreement with experiment is only qualitative, as expected.

The LDA eigenvalues and eigenfunctions form the input to the evaluation of the random phase approximation (RPA) screened Coulomb interaction W and of the GW self-energy Σ. Every matrix element of $W_{\mathbf{G},\mathbf{G}'}(\omega)$ is calculated at two imaginary energies, and the energy dependence fitted by a plasmon-pole model along the imaginary energy axis [6]. We evaluate the QP energies in first-order perturbation theory in $\Sigma - V_{xc}$ [4,5].

Our method for the calculation of the QP energies overcomes two of the main technical problems which have made similar calculations on real clusters unfeasible to date. The first point is the bottleneck represented by

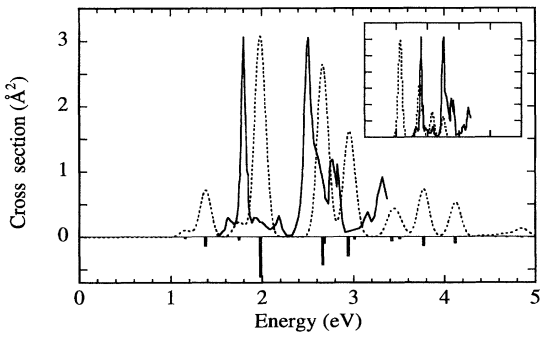

FIG. 2. Computed first-principles absorption spectrum of Na_4, including self-energy and excitonic effects. Our results (dotted line) are in arbitrary units, and a Gaussian broadening of 0.06 eV has been used. They are compared with experimental photodepletion cross sections obtained from Ref. [12]. Our unbroadened spectrum is also shown (vertical bars). In the inset, the LDA results are reported for comparison.

summations over the unoccupied states. In a traditional GW scheme, one has to determine a large number of empty states, which are summed over in the calculation of both W and Σ. It has recently been shown [16,17] that it is possible to calculate the DFT-RPA response function within the Dalgarno-Lewis scheme [18], which uses the closure relation in order to eliminate the need of an explicit knowledge of the empty states. In a similar way, our approach [19] eliminates the summation over empty states in the computation of the correlation part of the self-energy matrix elements.

The second problem is associated with the use of a supercell, in which the cluster, together with some surrounding vacuum, is repeated periodically to allow the use of a plane-wave basis set with all its computational advantages. Although this presents few problems in the DFT-LDA calculation (because the cluster is neutral, with no permanent dipole moment), in the GW calculation the additional electron (or hole) on the cluster induces charge fluctuations on the periodic images, resulting in a very slow convergence with supercell size. Our solution is to introduce a suitable cutoff of the spurious interaction between different supercells, *without modifying* the bare Coulomb form of the interaction inside the supercell itself. In addition to the complete elimination of the image interaction, this also turns out to simulate the effect of an improved Brillouin zone sampling for the integration of the interaction. Consequently, our DFT-LDA eigenvalues, QP energies, and exciton binding energies all converge at the same supercell size, almost as soon as the charge overlap becomes negligible. Since the computational time scales essentially as a^9, this represents a very considerable saving.

The cutoff is applied by simply suppressing the long-range tail of the Coulomb interaction beyond a distance c, which must be larger than the diameter of a sphere circumscribing the charge density of the cluster, and smaller than half the distance to the nearest-neighbor cluster. In Fourier space, this corresponds to a substitution of the Coulomb interaction $1/|\mathbf{q} + \mathbf{g}|^2$ with $[1 - \cos(c|\mathbf{q} + \mathbf{g}|)]/|\mathbf{q} + \mathbf{g}|^2$. Since, in this way, the interaction for $q \to 0$ is regularized, a substantial acceleration of the convergence with respect to the spacing of the $\mathbf{q}$ vectors is obtained as a by-product. Using a simple analytic model with Gaussian charge distributions, we have estimated that the volume of the supercell required to obtain an accuracy of 1% is reduced by 2 orders of magnitude using this cutoff. Moreover, clusters or molecules carrying a charge or a permanent dipole moment could be studied in the same scheme, introducing the cutoff already at the LDA level. Figure 3 shows the calculated GW correction to the energy of the LDA highest occupied state. The improved convergence with supercell size, when the spurious intercell interaction is properly switched off, is evident.

Using our approach, the calculation of the inverse dielectric function on a Cray C98 requires about 90 CPU

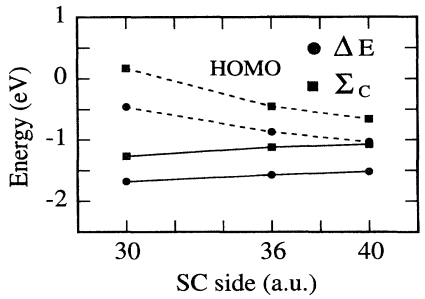

FIG. 3. Convergence, with respect to the supercell size, of the *GW* correction to the energy of the highest occupied LDA orbital (HOMO). The value of $\langle \Sigma_c \rangle$ is also shown. Dashed line: using the unaltered Coulomb interaction; solid line: after introduction of the spherical cutoff (see text).

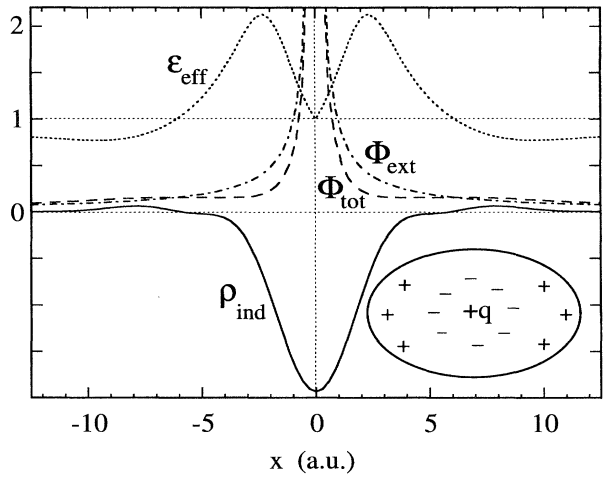

FIG. 4. Behavior of the induced charge $\rho_{\mathrm{ind}}(x)$ (solid line) due to a positive test charge at the center of Na_4, calculated from the RPA dielectric matrix, and plotted along the longer axis of the cluster. The unscreened $[\Phi_{\mathrm{ext}}(x)]$ and the total $[\Phi_{\mathrm{tot}}(x)]$ Coulomb potentials are also shown. The effective screening $\epsilon(x)$ is defined as their ratio. Note that at a distance of 5 a.u. the effective screening in metallic sodium would be already of the order of 50, whereas it has dropped to 1.2 in the cluster. The positively charged edges of the cluster (shown schematically in the inset) produce antiscreening, which causes the total potential to have a shallow minimum at $x \simeq 4$ a.u., becoming attractive at intermediate distances.

sec, while the time needed to compute the self-energy matrix elements is about 60 CPU sec per state. This very small computational expense allowed us to perform calculations of the full dielectric response at several finite frequencies, in order to check the plasmon-pole fit versus the calculated values of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\omega)$; the fit turns out to be very good.

The resulting QP spectrum is given by an almost rigid shift of the LDA eigenvalues. The *GW* corrections to the energies of the empty states are between 0.75 and 0.9 eV, while the HOMO and the lowest occupied state are lowered by 1.55 and 1.4 eV, respectively. The HOMO-LUMO gap, which is 0.55 eV in the LDA, becomes 3.0 eV, close to the Hartree-Fock (HF) value (about 3.4 eV) reported in Ref. [11]. Such large *GW* corrections are expected in a system in which screening is very weak, and to understand why it is weak we have calculated the linear response of our cluster to a point charge perturbation. As shown in Fig. 4, at small distances the screening is metal-like [the slope of $\epsilon(x)$ is $\simeq 0.5 \mathrm{a.u.}^{-1}$, to be compared with the Thomas-Fermi wave vector in bulk sodium, 0.786], but then an *antiscreening* effect appears, i.e., W is enhanced instead of decreased. This happens because the induced charge becomes positive near the cluster boundaries, as in a finite cluster (unlike a metal) the total charge within a finite volume must be conserved.

A related effect has been reported in tight-binding calculations for the silicon (111)-(2 × 1) surface [20] and in the C60 molecule [21], and is to be expected in finite, or low-dimensional, polarizable systems.

The weak screening also applies to the electron-hole interaction, so that excitonic effects are expected to be very important in optical absorption. In fact, as shown by the experimental spectrum in Fig. 2, absorption occurs at energies considerably lower than our QP gap.

In the calculation of the excitonic effects, we start from the QP energies, which are the appropriate one-particle levels. The exciton binding energies are then computed from a two-particle effective equation, which includes the screened electron-hole interaction as well as an unscreened exchange term [22]. The basis set for the exciton states is given by the products of the calculated occupied and empty LDA states, which is consistent with our use of first-order perturbation theory for the quasiparticle energies. We take for the screened electron-hole interaction the inverse dielectric matrix $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}$, already computed in the *GW* scheme. This properly describes local-field effects, which are very important in a small cluster. We neglect dynamical effects at this stage of the calculation, namely, the energy dependence of ϵ^{-1} [22,23]. Our scheme allows us to understand in detail the different contributions to the electron-hole interaction, and, in particular, the coupling of the various two-particle channels [24]. Moreover, our description of the exciton states may be directly compared with the results of multireference (double) CI calculations [11,24].

We now discuss the salient features of the calculated excitation spectrum. Figure 2 compares our results to experiment. Clearly, very good agreement is obtained for both the positions (within 0.2 eV) and the relative oscillator strengths of the main peaks. Self-energy corrections and excitonic effects both play crucial roles in the form of the spectrum. The final configurations of the excited states turn out to be an admixture of the electron-hole pairs found in the LDA scheme (see Fig. 1) [25].

The exciton wave functions corresponding to the three strongest peaks (at 2.0, 2.65, and 2.95 eV) show predominant contributions from the transitions between the LDA states $1b_{3u}$-$2a_g$ (2-4); $1a_g$-$1b_{2u}$ (1-3) and $1b_{3u}$-$1b_{1g}$ (2-6); $1a_g$-$1b_{1u}$ (1-5) and $1b_{3u}$-$1b_{2g}$ (2-8), respectively. The assignment of the main three absorption peaks to transitions from the ground state to states of symmetry B3u, B2u, and B1u, respectively, agrees well with the CI transitions (Table VI in Ref. [11]), which also contain the additional contribution of double excitations and core relaxation effects. The agreement is less good for the weak satellite peaks, which we find at lower energies (up to 1 eV) than the CI calculations. Those peaks, however, are very sensitive to the electron-hole exchange interaction, and hence to the localization, of the (LDA) one-particle wave functions. We have verified that the assignments, energies, and strengths of the main peaks are stable when we choose to start the whole calculation from HF instead of LDA results, or when we slightly change the interatomic distances [26]. However, the satellite peaks move considerably (0.2–1.0 eV) when we start from HF and also change their oscillator strengths. A change in the interatomic distances, instead, affects only the intensities of the satellites. Future calculations will therefore include self-consistently calculated quasiparticle wave functions. We also plan to include the effects of dynamical screening in the excitonic calculations, which are expected to be important for low-lying excitonic states whose binding energy is of the order of the band gap.

In summary, we have shown that *ab initio GW* calculations of quasiparticle energies in real clusters are now feasible, by using a new, efficient technique to avoid the empty-state summations in the calculation of self-energy corrections, and a method which eliminates the problem of slow convergence with supercell size, and is also applicable to cluster supercell calculations in contexts outside *GW*. Screening in small metal clusters is dramatically different from that in the infinite metal and gives rise to strong excitonic effects, which we have evaluated from first principles, starting from the *GW* QP energies and the DFT-LDA wave functions. This allows the *ab initio* computation of the absorption spectrum of the cluster, and an assignment of the main features which are in good agreement with experiment and with CI calculations. Our method does not suffer from the limitation of CI to very small aggregates, since it scales with the system size essentially as $N^3 \ln(N)$ instead of N^5. Moreover, a physically transparent and detailed picture of the different contributions to the excitation spectrum emerges.

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[1] For a review, see, for example, R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).
[2] L. Hedin and S. Lundqvist, Solid State Phys. **23**, 1 (1969).
[3] L. Hedin, Phys. Rev. **139**, 796 (1965).
[4] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986).
[5] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys Rev. B **37**, 10 159 (1988).
[6] R. W. Godby and R. J. Needs, Phys. Rev. Lett. **62**, 1169 (1989).
[7] J. P. A. Charlesworth, R. W. Godby, and R. J. Needs, Phys. Rev. Lett. **70**, 1685 (1993); E. L. Shirley and S. G. Louie, *ibid.* **71**, 133 (1993).
[8] S. Saito, S. B. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. B **40**, 3643 (1989).
[9] W. Andreoni, Z. Phys. D **19**, 31 (1991).
[10] V. Bonacic-Koutecky, J. Pittner, C. Scheuch, M. F. Guest, and J. Koutecky, J. Chem. Phys. **96**, 7938 (1992).
[11] V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, J. Chem. Phys. **93**, 3802 (1990); Chem. Phys. Lett. **166**, 32 (1990).
[12] C. Wang, S. Pollack, D. Cameron, and M. M. Kappes, J. Chem. Phys. **93**, 3787 (1990).
[13] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[14] U. Rötlisberger and W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).
[15] A. K. Ray, Solid State Commun. **71**, 311 (1989).
[16] S. Baroni and A. Quattropani, Nuovo Cimento Soc. Ital. Fis. **5D**, 89 (1985); S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).
[17] A. A. Quong and A. G. Eguiluz, Phys. Rev. Lett. **70**, 3955 (1993).
[18] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London A **233**, 70 (1955).
[19] L. Reining, G. Onida, and R. W. Godby (unpublished).
[20] L. Reining and R. Del Sole, Phys. Rev. B **44**, 12 918 (1991).
[21] O. Gunnarson, D. Rainer, and G. Zwicknagl, Int. J. Mod. Phys. B **6**, 3993 (1992).
[22] L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966).
[23] G. Strinati, Phys. Rev. Lett. **49**, 1519 (1982).
[24] G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni (unpublished).
[25] Fully converged results are achieved, including 160 basis functions in the exciton diagonalization.
[26] In particular, this is true for bond lengths increased by 6%, corresponding to the HF geometry (Ref. [11]).