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**Time-Dependent Density-Functional Theory** 



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## Optical and magnetic properties of boron fullerenes

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We report linear response properties of the recently proposed boron fullerenes [N. Gonzalez Szwacki *et al.*, *Phys. Rev. Lett.*, 2007, **98**, 166804]: magnetic susceptibilities, static dipole polarizabilities and dynamical polarizabilities (*i.e.* optical and near ultraviolet absorption spectra), calculated from first principles within the (time-dependent) density-functional theory framework. We find that all clusters except  $B_{80}$  are diamagnetic. The strong cancellation between diamagnetic and paramagnetic currents in  $B_{80}$  leads to a very small value for its susceptibility that turns out to be slightly paramagnetic. Static polarizabilities increase linearly with the number of B atoms. Furthermore, the absorption spectrum of  $B_{80}$  is very different from the one of its carbon counterpart  $C_{60}$ , exhibiting a low absorption threshold of about 1.5 eV and many peaks in the visible and near ultraviolet. This can be understood by the analysis of the wavefunctions involved in the low energy transitions.

### I. Introduction

The hollow carbon clusters, or "fullerenes", were only theoretical predictions<sup>1–3</sup> for two decades, until their discovery in 1985.<sup>4</sup> Recently, Gonzalez Szwacki *et al.*<sup>5</sup> have predicted the existence of a boron *doppelgänger* of the C<sub>60</sub> fullerene: a B<sub>80</sub> cage whose experimental detection seems quite likely in the near future. Indeed, the nanotubular boron structures were also suggested by first-principles calculations,<sup>9</sup> and later confirmed experimentally.<sup>10</sup> In the same vein, we should also refer the new boron sheets proposed in ref. 11, and the corresponding nanotubes proposed in ref. 12, that use the same fundamental motif as the B<sub>80</sub> cluster.

Like  $C_{60}$ ,  $B_{80}$  has a remarkable stability (as measured, for example, by its cohesive energy), a relatively large energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), and, like  $C_{60}$ , *almost I*<sub>h</sub> symmetry; even though the original work of Gonzalez Szwacki *et al.* reported an icosaehedral shape, they acknowledged the existence of several close local minima at distorted geometries. Later it has been defended that the geometry of the most stable structure seems to be a slight distortion of the  $I_h$  configuration. Both Gopakamur *et al.*<sup>6</sup> and

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Baruah *et al.*<sup>7</sup> have further investigated the stability of the lowest energy isomers of  $B_{80}$ , and claim that the icosahedral structure is unstable; the ground state configuration is reported to have, in fact,  $T_h$  symmetry. However, the recent work of Sadrzadeh *et al.*<sup>8</sup> has also investigated the issue, and report very small energy differences (lower than 30 meV) among the three lowest lying isomers ( $I_h$ ,  $T_h$ , and  $C_1$ ), with the icosahedral shape being, in fact, a close winner.

Unlike  $C_{60}$ ,  $B_{80}$  accommodates one boron atom in the center of each hexagon, accounting for the extra 20 atoms; this hexagon reinforcement is necessary to stabilize the otherwise unstable icosahedral  $B_{60}$  cage. In this manner, the *Aufbau* principle proposed by Boustani<sup>13</sup> is respected: stable homoatomic boron clusters are constructed with two basic bricks: hexagonal pyramids,  $B_7$  (characteristic of convex and quasiplanar clusters), or pentagonal pyramids,  $B_6$  (characteristics of open-spherical clusters, such as the prototypical  $B_{12}$ ). Alternatively,  $B_{80}$  can also be viewed as six interwoven  $B_{20}$  double-rings;<sup>5</sup> the inclusion of staggered double rings in the structure of boron clusters seems to enhance their stability



Fig. 1 Structures of the boron cages studied in this work.

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(see Fig. 1, where, among other structures, both the  $B_{20}$  double-ring cluster and the  $B_{80}$  are depicted).

The existence of cage-like boron conformations should come as no surprise, given the rich chemistry of this element: boron nanostructures have been found in very diverse forms—clusters,<sup>14–21</sup> nanowires<sup>22</sup> or nanotubes.<sup>10,23,24</sup> The family of boron nanostructures is unlimited, since boron has the property of catenation: it can form structures of arbitrary size by linking covalent bonds with itself—a property only shared with carbon. In fact, a wide variety of polyhedral clusters containing boron have been known for a very long time, and have been used for a surprisingly large number of applications.<sup>25</sup> The rich diversity can be explained in terms of the high coordination number and the short covalent radius usually exhibited by boron, which leads to the possibility of creating strong directional bonds with many elements.

Before the work of Gonzalez Szwacki and collaborators<sup>5</sup> on  $B_{80}$  and other possible hollow structures,<sup>14</sup> a significant amount of work had been reported on smaller, homoatomic boron clusters: Experimental work<sup>15-17,20</sup> and calculations<sup>13,15,17,20,26–32</sup> that, led to one main conclusion regarding the structures: small clusters appear typically in either convex, quasi-planar, spherical or nanotubular shapes. This is surprising, since bulk boron, in its typical phases, is constructed from the icosahedral  $B_{12}$  unit. Below 20 atoms, the most stable shapes are planar, whereas tubular structures start to become more stable above this number.<sup>20</sup> Recently, some of us<sup>33</sup> contributed to the possible elucidation of the precise planar-to-tubular transition by calculating the optical absorption of the main conformers: The spectra show significant differences among them, possibly enabling the optical characterization of mass selected samples of boron clusters with unknown geometry.

Until experimentalists find a way to produce boron fullerenes, first-principle calculations remain the only route to understanding their properties. In this work we report on the linear response signatures of  $B_{80}$  and some of the other stable fullerenes proposed by Gonzalez Szwacki *et al.*: dynamical polarizabilities, static dipole polarizability and magnetic susceptibilities.

The importance of the knowledge of the static dipole polarizability is beyond doubt (*e.g.* it is a coarse indicator of molecular shape, it determines the long-range interaction between molecules, *etc.*), as it is the case for its dynamical generalization (*e.g.* the excitation energies are determined by the peak positions of this function; the absorption cross section is trivially related to the imaginary part of the dynamical polarizability, *etc.*).

Furthermore, it is interesting to realize if boron fullerenes share the anomalous magnetic properties present in traditional carbon fullerenes. The nature and magnitude of the electronic ring currents that circulate around the carbon rings is intriguing; Elser and Haddon<sup>34,35</sup> calculated the contribution of these ring currents to the magnetic susceptibility by making use of London's theory.<sup>36</sup> The finding was surprising since this contribution was found to be vanishingly small; this result was later backed by the experiment:<sup>37</sup> the measured susceptibility had almost the same value as the estimated local contributions to the diamagnetism, which implies a small ring current contribution. However, this fact does not imply that currents do not circulate around the carbon cycles; the truth is that fullerenes exhibit both diamagnetic and paramagnetic ring currents, which cancel each other.<sup>38</sup> This result is surprising if we attempt to explain the ring current induced magnetism with a more naïve approach—such as Pauling's model.<sup>39</sup>

It is then clear how the phenomenon of ring currents usually linked to the "aromatic" character of a molecule—and its effect on the magnetic susceptibility of clusters, can be subtle. The "spherical aromaticity" of fullerenes, <sup>40</sup> in particular, demands for a careful theoretical study of the magnetic response. Boron clusters, including boron fullerenes, also contain rings of delocalized  $\pi$  orbitals, and its aromatic character has also been discussed.<sup>41,42</sup> It is therefore in order to investigate, at an accurate level of theory, the magnetic properties of the newly proposed B<sub>80</sub> and its family of fullerenes.

## II. Methodology

The cluster geometries are those reported by Gonzalez Szwacki *et al.*,<sup>5</sup> the ones optimized within the density-functional theory (DFT) framework with the Perdew–Burke–Ernzerhof<sup>43</sup> (PBE) parametrization. The core electrons were frozen thanks to the ultrasoft Vanderbilt pseudopotentials.<sup>44</sup> The minimized geometries, which we used without further relaxation are depicted in Fig. 1. Besides the cage solutions, we include, for completeness, the prototypical  $B_{20}$  ring.

We then performed density-functional perturbation theory<sup>45</sup> in order to obtain the static magnetic susceptibilities, finite-differences to calculate the static polarizabilities, and time-dependent density-functional theory (TDDFT)<sup>46</sup> in order to obtain the optical absorption spectra. In all cases we used the code Octopus.47,48 The most salient features of this approach are: the relevant functions (Kohn-Sham wave functions, densities) are discretized on a real-space regular mesh; the ion-electron interaction is modelled with normconserving pseudopotentials.<sup>49</sup> The grid spacing was chosen to be 0.18 Å, and the simulation boxes were built large enough to ensure the convergence of the results-in practice, by placing the box boundaries at least 5 Å away from the closest atom. In all calculations, we approximated the exchange and correlation functional by the PBE<sup>43</sup> parametrization. The HOMO-LUMO gaps calculated in this way are shown in Table 1, and are in very good agreement with previously published results.5

Regarding the calculation of the dynamical polarizabilities, we employed a real-time TDDFT approach, based on the explicit propagation of the time-dependent Kohn–Sham equations. In this approach, one first excites the system from its ground state by applying a delta electric field  $E_0\delta(t)\mathbf{e}_m$ (the unit vector  $\mathbf{e}_m$  determines the polarization direction of the field, and  $E_0$  its magnitude, which must be small to ensure that the response is linear). The Kohn–Sham equations are then propagated forward in real time,<sup>50</sup> and the time-dependent density  $n(\mathbf{r},t)$  readily computed. From this quantity one can then obtain the absorption cross-section as explained in ref. 47, 51 and 52. In this work, the total propagation time

**Table 1** HOMO–LUMO gaps (H–L in eV), ionization potentials (IP in eV) calculated through total energy differences, magnetic susceptibilities ( $\chi$  in cgs ppm mol<sup>-1</sup>), static dipole polarizabilities ( $\alpha$  in Å<sup>3</sup>), and static dipole polarizabilities per number of boron atoms for the selected boron clusters. For these two latter quantities, we present both average values (*e.g.*,  $\bar{\chi} = \text{Tr } \chi/3$ ) and anisotropies (*e.g.*,  $\Delta \chi = \sqrt{[3\text{Tr } \chi^2 - (\text{Tr } \chi)^2]/3}$ )

	H–L	IP	$\bar{\chi}$	$\Delta \chi$	$\bar{\alpha}$	$ar{lpha}/N$	Δα
$B_{20}(r)$	1.45	7.5	-250.2	330.1	44.0	2.20	18.2
B <sub>38</sub>	0.95	7.4	-468.3	37.7	73.8	1.94	12.3
B <sub>44</sub>	0.96	7.3	-614.4	156.3	83.1	1.89	15.0
B <sub>80</sub>	1.01	6.6	219.3	3.9	147.9	1.85	0.5
B <sub>92</sub>	1.07	6.5	-831.3	0.8	162.6	1.77	0.01

was chosen to be  $30\hbar/eV \approx 20$  fs, and the time step  $0.002\hbar/eV \approx 1.3$  as. This approach has already been used for many cluster and molecular systems: metal and semiconducting clusters,<sup>53–56</sup> aromatic hydrocarbons,<sup>52,57,58</sup> or protein chromophores.<sup>59,60</sup> The accuracy to be expected from this technique is around 0.1–0.2 eV for the position of the spectral peaks in the visible and near ultraviolet wavelength interval.

Regarding the calculation of the magnetic susceptibilities, we have employed density-functional perturbation theory the reformulation of Sternheimer's equation within the DFT framework.<sup>45</sup> Details of our specific implementation can be found in ref. 61. Note that due to the use of non-local pseudopotentials, special care has to be taken in order to ensure the gauge invariance of the underlying equations. To solve this problem, we used the GIPAW approach of Pickard and Mauri.<sup>62</sup>

### III. Results

We start the discussion of our results by the magnetic susceptibilities (see Table 1). With the exception of  $B_{80}$ , all clusters studied are diamagnetic, with the absolute value of the susceptibility increasing with the number of atoms. Furthermore, the magnetic susceptibility tensor is quite isotropic for most fullerene-like clusters, reflecting the global symmetry of these systems. The exception is obviously the ring isomer of  $B_{20}$ , and to a lesser extent  $B_{44}$ .

For  $B_{80}$  we find a completely different situation, with the fullerene being now slightly paramagnetic ( $\bar{\chi} = 219.3 \text{ cgs ppm mol}^{-1}$ ). The small absolute value for the susceptibility indicates that there is indeed a strong cancellation between the paramagnetic and diamagnetic currents. This value should be compared to  $C_{60}$  (which has a susceptibility of about  $-260 \text{ cgs ppm mol}^{-1}$ ).<sup>37,38</sup> In the  $C_{60}$  case, the reason for the small diamagnetism is the negligible value of the ring current susceptibility (the  $\pi$ -electron contribution to the susceptibility); the paramagnetic and diamagnetic ring currents circulating around the pentagons and hexagons, respectively, cancel each other. In the case of  $B_{80}$ , the geometry is more complex with boron atoms occupying the center of the hexagons, complicating this simple picture, and leading to a slightly larger value of the paramagnetic current relatively to the diamagnetic term.

Note, however, that like for  $C_{60}$  the total value for magnetic susceptibility of  $B_{80}$  depends strongly on the geometry and in particular on the ratio between different B–B bond lengths. Changing the bond lengths alters the equilibrium between the

diamagnetic and paramagnetic contributions: as these contributions are both large and with different signs, but more or less of the same magnitude, their sum depends strongly on small variations of their individual values. To study this effect, we calculated the magnetic susceptibility for the three geometries optimized with the B3LYP functional in ref. 5. We found 42.8 cgs ppm mol<sup>-1</sup> for the  $I_{\rm h}$  geometry, 46.2 cgs ppm  $mol^{-1}$  for the  $C_1$ , and 29.7 cgs ppm  $mol^{-1}$  for the  $T_h$ . The differences can be explained by looking at the different B-B bond lengths. For all structures the length of the bonds connecting the atoms in the center of the hexagons to their neighbors is around 1.70 Å (with some dispersion especially in the  $T_{\rm h}$  geometry). However, for the other two bond-lengths,  $d_{\rm h}$  measuring the side of the hexagons and  $d_{\rm p}$  measuring the side of the pentagons, we can see how the different exchangecorrelation functionals influence the structure. For the cluster optimized with the PBE we find  $d_{\rm h} \sim 1.68$  Å and  $d_{\rm p} \sim 1.73$  Å, while the B3LYP yields a small contraction of the side of the hexagon to  $\sim 1.67$  Å and a small expansion of the pentagons to  $\sim 1.74$  Å. These are very small differences, but due to the subtle cancellation between the paramagnetic and diamagnetic currents leads to a large difference in the susceptibility.

Looking at the values for the static polarizability we see that they increase essentially linearly with the number of boron atoms, with a slope of approximately 2 Å<sup>3</sup> per atom. The slope, however, decreases slightly with increasing number of atoms. This simple result reflects the fact that, as all boron atoms in these clusters have a similar chemical environment, the static polarizability is mainly additive and determined by the overall size of the cluster.

More insight can be obtained from the dynamical polarizability, in particular from the optical absorption cross section spectra given in Fig. 2. The low energy spectrum of  $B_{20}$ "double ring" isomer<sup>33</sup> is characterized by well defined peaks, and is dominated by one sharp peak at around 4.8 eV-which originates from electron fluctuations perpendicular to the cylinder axis. The absorption strength is suppressed below 4 eV (with the exception of a couple of small peaks) as the low energy transitions are dipole forbidden. The spectra of B<sub>38</sub>, B<sub>44</sub> are not so well defined-there are many peaks whose respective widths overlap, creating a broad, structureless response whose onset is below 2 eV. This fact can also be rationalized by looking at their geometries: these clusters are not so symmetric (distorted  $D_3$  and distorted  $D_{3h}$  for  $B_{38}$ ,  $B_{44}$ , respectively), and have a larger distribution of bond lengths. The most stable of the clusters studied, B<sub>80</sub>, also has some weak absorption peaks in the visible, although the strongest peaks are positioned at



**Fig. 2** Absorption cross section (in Å<sup>2</sup>) for  $B_{20}$  (ring isomer),  $B_{38}$ ,  $B_{44}$ ,  $B_{80}$  ("slightly-off"  $I_h$ ), and  $B_{92}$  as predicted by TDDFT. Most of the energy range shown is below the calculated ionization potential of these clusters (see Table 1).

energies higher than 3 eV. Finally, the absorption cross section of the largest fullerene studied here,  $B_{92}$ , is qualitatively similar to  $B_{80}$ .

It is curious to compare the results for  $B_{80}$  to the known absorption spectrum of its carbon counterpart  $C_{60}$ . The latter is dominated by a  $\pi$ -plasmon at around 6.3 eV<sup>63</sup> and has a large optical gap of more than 3 eV. This is also the typical absorption spectrum of the planar polycyclic aromatic hydrocarbons.<sup>57,58</sup> On the other hand,  $B_{80}$  exhibits a much



**Fig. 3** Kohn–Sham states of the  $B_{80}$  clusters. The states HOMO – 1, HOMO – 2, HOMO – 3, and HOMO – 4 are nearly degenerate with the HOMO, and very similar to the HOMO. Also LUMO + 1 is similar to LUMO, so it is not displayed here. The magenta (cyan) isosurface corresponds to the positive (negative) part of the wave functions.

smaller optical gap (of around 1.5 eV) and a much less structured spectrum. This can be explained by two factors. First the HOMO–LUMO gap of  $C_{60}$  (around 1.6 eV) is larger than the one of  $B_{80}$  (around 1 eV). Looking at the Kohn–Sham states of  $B_{80}$  around the HOMO–LUMO gap reveals the second factor (see Fig. 3).

The HOMO state (and the other states immediately below) are located around the three  $B_{20}$  rings and retain a certain " $\pi$ -like" character, *i.e.* the wave-functions change sign going from outside to inside the cage. The first occupied state of different character is the HOMO-5, that is mainly located around the pentagons, but spreading considerably to other regions of the cluster. The situation is considerably more complicated for the LUMO states: they are no longer of " $\pi$ -like" symmetry, and extend over considerable regions of the cluster. It is then clear that the dipole matrix elements between the lowest occupied and unoccupied states will not vanish (as it happens, *e.g.*, for the B<sub>20</sub> ring), and absorption will start shortly after the HOMO–LUMO gap.

#### IV. Conclusions

We performed first-principle calculations of electrical and magnetic linear response properties of the boron fullerenes recently proposed by Gonzalez Szwacki *et al.*<sup>5</sup> In particular, we investigated the signatures of the counterpart of  $C_{60}$ , the  $B_{80}$  cage, the most stable of these clusters.

Regarding the magnetic response, all clusters except  $B_{80}$  turn out to be diamagnetic. On the other hand,  $B_{80}$  turns out to be slightly paramagnetic. This arises from the presence of a strong cancellation between diamagnetic and paramagnetic effects, as it is known to happen in the carbon fullerene.

The static polarizability increases monotonically with the number of boron atoms. More precisely, it is roughly proportional to the number of atoms, pointing to an additive behavior justified by the fact that boron atoms in all clusters studied here have a similar chemical environment. The absorption spectra of the boron cages display similar features, with absorption thresholds close to the HOMO–LUMO gaps and many peaks overlapping in the visible and near ultraviolet region. On the other hand, the optical spectrum of the double-ring  $B_{20}$  is dominated by large peaks above 4 eV, while absorption is suppressed at low energies due to the presence of many dipole forbidden transitions.

The physical properties of boron fullerenes, and in particular of the stable  $B_{80}$  are by now fairly well described and understood through theoretical calculations. Unfortunately, these clusters have not been produced experimentally yet. It is however our belief that, like for  $C_{60}$  and the carbon nanotubes before, the experimental ingenuity will lead in the near future to the creation and detection of these interesting nanostructures.

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