PHYSICAL REVIEW B VOLUME 44, NUMBER 23 15 DECEMBER 1991-I

Local approach to calculate total energies in semiconductors beyond the Hartree-Fock approximation

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(Received 30 July 1991)

We present a method to calculate the total energy in semiconductors. The kinetic, Coulomb, and exchange contributions to the energy are calculated exactly within a finite cluster of atoms. The electronic correlation energy is included *a posteriori* via a local-density-functional approximation. The calculated electronic density for large enough clusters of atoms is in excellent agreement with experimental data for crystals. The method is tested against the H_2 molecule with excellent results and then applied to silicon and interstitial oxygen in silicon. The local aspects of the electronic correlation are discussed in detail.

I. INTRODUCTION

The problem of the calculation of the total electronic energy in molecules and solids has been addressed from different approaches in the past decades. The problem is indeed important since it allows the determination of equilibrium atomic geometries and therefore the ground-state properties of the system. The main difficulty in the total electronic energy calculation is the proper treatment of the electronic correlations. To handle the calculation of the correlation energy the most widely used approaches have been based on the density-functional formalism[1] in its local-density-approximation (LDA) version.[2] This method presents several important advantages that make it flexible and suitable for application to many different and complicated systems.[2] In its more widespread versions, the LDA not only makes a local-density approach for the correlation energy, but also the exchange energy is approximated by a local functional. The overwhelming successful results obtained with this approximation are, to some extent, due to the partial compensation between the underestimated exchange and the overestimated correlation energy contributions. This probably is one of the major weaknesses of the method although several attempts, beyond the local-density approximation,[2] have been made to overcome it.

In this work we develop a method in which the kinetic, Coulomb, and exchange energies are calculated exactly [i.e., the Hartree-Fock (HF) energy] whereas the correlation energy is calculated by means of the LDA taking proper account of the self-correlation terms. The method, which is similar in spirit to the one developed by Casua and co-workers,[3,4] is applied in this work to clusters although in principle it can be extended to infinite systems.

This work is organized as follows. In Sec. II we discuss the method and apply it to the H_2 molecule to test it. Also in this section we calculate the electronic structure of clusters of silicon atoms within the Hartree-Fock approximation; once a good electronic charge density is obtained the correlation energy is calculated. In Sec. III the local character of the correlation energy is discussed in two specific problems, namely, pure silicon and interstitial oxygen in silicon. Finally, in Sec. IV the conclusions of the work are summarized.

II. METHOD OF CALCULATION

In this section we describe the method of calculation for two different systems, namely, the H_2 molecule for which exact results[5] to compare with are available and silicon where only approximated calculations of the correlation energy are possible.

A. The H_2 molecule

To discuss the method of calculation and show how it works we will concentrate in this section on the H_2 molecule in which most of the expressions can be written in closed form and exact results are available in the literature.

We start with one $1s$ atomic orbital per hydrogen atom of the form

$$\phi(\mathbf{r})=(\xi^3/\pi)^{1/2}e^{-\xi r} , \tag{1}$$

where ξ is a variational parameter. To solve the H_2 molecule in the restricted Hartree-Fock approximation we construct the bonding molecular orbital

$$\psi_b(\mathbf{r})=\frac{1}{(2+2S)^{1/2}}\{\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\} , \tag{2}$$

where S is the overlap between the orbitals in the two atoms. The total energy can then be written as

$$E_{\mathrm{HF}}=H_k+H_C+H_x . \tag{3}$$

H_k, H_C, and H_x stand for the kinetic, Coulomb, and exchange energies, respectively, and have the form

$$H_k=\sum_{\mu\nu} P_{\mu\nu}H^{\mathrm{core}}_{\mu\nu} , \tag{4}$$

H^{core} being the Coulomb potential produced by the nuclei,

$$H_C=\frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\nu|\lambda\sigma)\ , \tag{5}$$

$$H_x=-\frac{1}{4}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\lambda|\nu\sigma)\ . \tag{6}$$

$P_{\mu\nu}$ are the matrix elements of the density operator, i.e.,

$$P_{\mu\nu}=2\sum_{i}^{\text{occ}} c_{\mu i}c_{\nu i}\ , \tag{7}$$

where the $c_{\mu i}$ is the coefficient of the orbital μ in the molecular orbital labeled i and $(\mu\nu|\lambda\sigma)$ are the two electron integrals of the form

$$(\mu\nu|\lambda\sigma)=\int\int \phi_\mu(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)|\mathbf{r}_1-\mathbf{r}_2|^{-1} \times\phi_\lambda(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\ . \tag{8}$$

With the above basis set the total (electronic plus nuclear) energy can be written in a closed form as a function of the atom's separation R. The minimum energy is at $R=0.735$ Å with an energy of -30.689 eV, the exponent coefficient ξ of the 1s orbital being 1.19. This is a very well-known result which, as far as the energy is concerned, is far from the exact value of -31.947 eV. One can also perform the same calculation using the local-density approximation. The results for the exchange-correlation functionals of Gunnarsson and Lundqvist[6] (GL) and Vosko and co-workers[7,8] (VWN) are given in Table I.

One natural way to improve the Hartree-Fock result is by including the electronic correlation corresponding to the Hartree-Fock charge density assuming it is close to the actual charge distribution in the H_2 molecule. This contribution can be easily calculated with the result that, at the Hartree-Fock equilibrium distance, the calculated correlation energy is -3.165 and -2.598 eV for the GL and VWN density functionals, respectively. If this energy is added to the above Hartree-Fock result we end up with a total energy which is much lower than the exact value. The main source of error of the above calculation is the fact that we have included, when using the LDA, the interaction of each electron with itself. This spurious interaction should be subtracted from the above calculation. To do this we consider the correlation of each single electron in each occupied molecular orbital; this self-correlation energy is -1.114 and -1.343 eV for the GL and VWN functions, respectively. In this way the electronic correlation reads

$$E_c=\int\rho(\mathbf{r})\varepsilon_c[\rho(\mathbf{r})]d\mathbf{r}-\sum_{\sigma=\uparrow,\downarrow}\int\rho^{\sigma}(\mathbf{r})\varepsilon_c[\rho^{\sigma}(\mathbf{r})]d\mathbf{r}\ , \tag{9}$$

where $\rho(\mathbf{r})$ and $\rho^{\sigma}(\mathbf{r})$ are the electron density of the H_2 molecule and the charge of one electron in the occupied molecular orbital [Eq. (2)]. ε_c stands for the functional of the correlation energy density.

The result for the total energy is now -31.829 and -32.031 eV for the GL and VWN functionals, respectively. These results are in excellent agreement with the exact result of -31.947 eV. Also for the binding energy we obtain the values of 4.629 eV and 4.831 eV, respectively, as compared with the exact result of 4.747 eV. The LDA also gives good results for the binding energy of the H_2 molecule, the values being 4.79 and 4.91 eV for the GL and VWN functions, respectively.

TABLE I. Calculated parameters of the H_2 molecule along with the exact (experimental, Ref. 5) results. Distances are in Å and energies in eV.

	R	ξ	Total energy
HF	0.73	1.19	-30.69
LDA (VWN)	0.77	1.17	-30.86
LDA (GL)	0.76	1.17	-31.40
This work (VWN)	0.73	1.20	-32.03
This work (GL)	0.73	1.20	-31.83
Experimental	0.74		-31.95

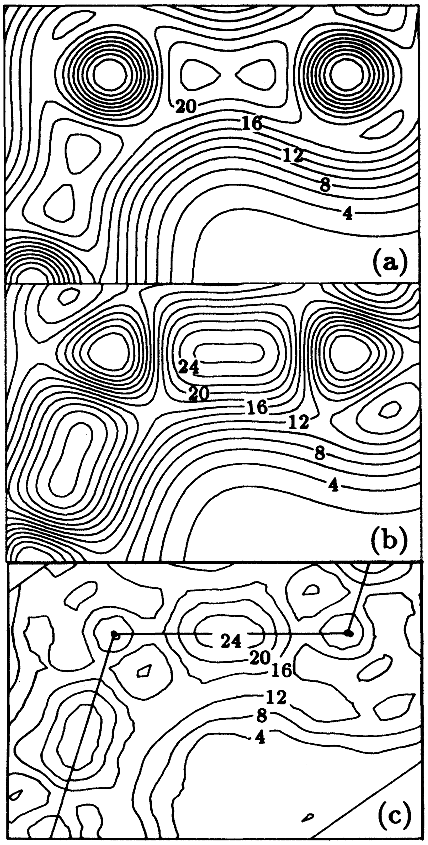

FIG. 1. Electronic charge distribution in silicon. (a) Calculated total electronic charge distribution for the Si_8H_{18} cluster for the minimal basis set. (b) Calculated charge distribution for the Si_8H_{18} cluster for the ten orbitals per silicon atom basis set. (c) Experimental results of Ref. 10. The units are electrons per crystal unit cell.

B. Silicon

The fact that the above method works for the H_2 molecule does not guarantee it can successfully be applied to more complicated systems. To show the applicability of the method we describe in this section the results for silicon.

We consider first a cluster of eight silicon atoms in the tetrahedral coordination properly saturated with hydrogenlike atoms to simulate the rest of the silicon crystal. We perform a complete restricted Hartree-Fock calculation in this cluster for the valence electrons while the effect of the core electrons is simulated by a proper nonlocal pseudopotential.[9] Since the aim of the method of calculation is to include the correlation energy by using the local-density approximation an accurate electronic charge distribution is needed. In Fig. 1 we show the charge density obtained for the cluster at the equilibrium distance (2.31 Å) along with the experimental data.[10] For the sake of comparison we present the results for a minimal basis (one 3*s* and three 3*p*) orbitals and for a more complete ten-orbital basis set (one 3*s*, three 3*p*, five 3*d* and one 4*s*) used throughout this work. In Fig. 1 it is clearly seen that a good basis set is needed to obtain an accurate charge distribution. From this result two important facts should be noticed: (a) the charge density obtained with the Hartree-Fock calculation is very close to the correct charge density, and (b) a finite cluster of atoms properly saturated reproduces the experimental electronic charge density of the infinite crystal. To stress this point we have plotted in Fig. 2 the crystal energy eigenvalues distribution obtained from the cluster Hamiltonian matrix elements in the manner described elsewhere.[9] As we can see the band structure obtained for the ten orbitals per atom basis with the information provided by the cluster calculation reproduces fairly well the Hartree-Fock band structure obtained by other methods.[11,12]

To calculate the correlation energy we proceed as for the H_2 case. The full correlation energy is obtained by integration of the density-correlation functional weighted by the total charge density. This calculation has been performed using the VWN functional (for the GL functional the results are similar) and for various separations of the cluster Si—Si bonds. The total correlation energy is almost constant being −65.716 eV (−80.255 eV for the GL functional) at a 2.31-Å separation. In order to take proper account of the self-correlation correction we have calculated the the correlation energy of each electron in the different molecular orbitals. In this way the

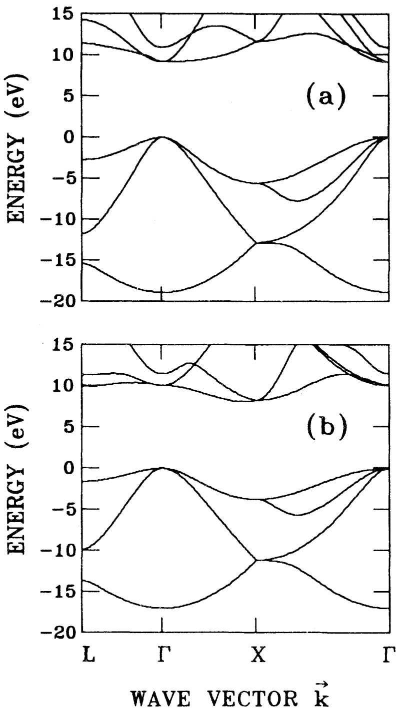

FIG. 2. Hamiltonian eigenvalue dispersion vs wave vector along the crystal main symmetry directions. (a) Results for the minimal basis set. (b) Results for the ten orbitals per silicon atom basis.

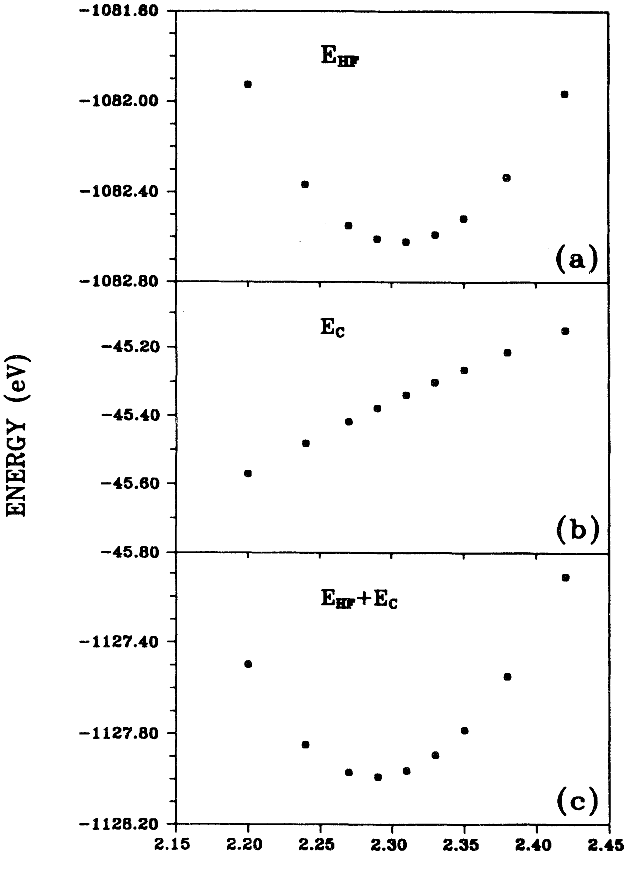

FIG. 3. Different contributions to the total energy vs silicon-silicon distance in the Si_8H_{18} cluster. (a) Hartree-Fock result. (b) Correlation energy after subtracting the self-correlation terms [Eq. (10)]. (c) Final total energy.

correlation energy is

$$E_c=\int\left[\rho(\mathbf{r})\varepsilon_c[\rho(\mathbf{r})]-\sum_{n}^{\text{occ}}\sum_{\sigma=\uparrow,\downarrow}\rho_n^{\sigma}(\mathbf{r})\varepsilon_c[\rho_n^{\sigma}(\mathbf{r})]\right]d\mathbf{r}\;, \tag{10}$$

where the sum is extended to all the occupied molecular orbitals and $\rho_n^{\sigma}(\mathbf{r})$ is the electronic charge of one electron in a particular molecular orbital n. The second term in Eq. (10) is the self-correlation correction. At the HF equilibrium distance of 2.31 Å the self-correlation energy is -20.377 eV, which has to be subtracted from the above result giving a correlation energy of -45.339 eV (-48.211 eV for the GL functional). We notice that the self-correlation entails approximately 30% of the total correlation energy as in the H_2 molecule. The results of the calculations for different separations of the silicon atoms are displayed in Fig. 3. The correlation energy does not depend very much on the atomic separation near equilibrium [see Fig. 3(b)] being larger for shorter separations of the silicon atoms as in the H_2 molecule. Its main effect when added to the Hartree-Fock energy is to shift the equilibrium position to shorter distances, in this case from 2.31 to 2.29 Å.

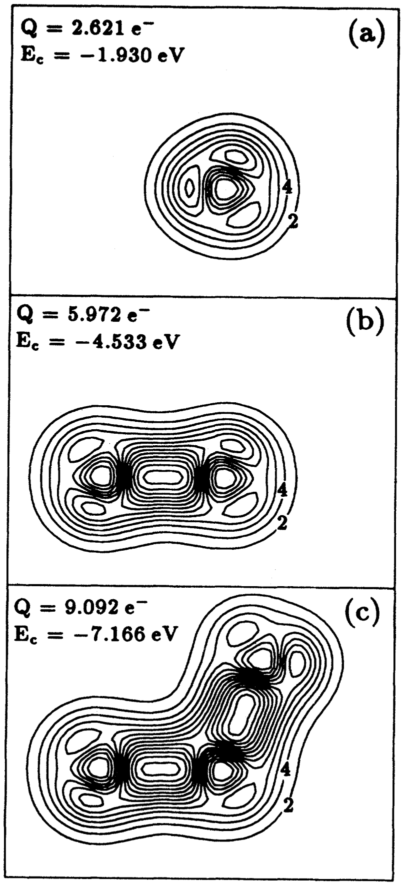

FIG. 4. Partial electronic charge distributions and the corresponding correlation energies (see the text for the definitions) of silicon in the Si_8H_{18} cluster. (a) Atomic charge contribution. (b) Charge contribution from nearest-neighbor silicon atoms. (c) Charge contribution from nearest- and next-nearest-neighbor silicon atoms. The units are electrons per bulk silicon unit cell. The total charge contained in each partial distribution is indicated.

In order to test the above results for silicon we can compare them with other calculations. In particular we can compare with the results obtained by Ganduglia-Pirovano *et al.*[13] using the local ansatz.[14] To do this we have to analyze the intra-atomic and interatomic correlations, which is done in Sec. III.

III. LOCAL ASPECTS

Once the total correlation energy is obtained it is important to study to what extent it depends on the local charge distribution. For this purpose we have calculated the partial correlation energy due to partial charge contributions of the total charge. Since we are working with a local basis set this can be unambiguously defined. We define the correlation energy related to a set of atoms $\{s\}$ as the correlation energy of the electronic charge associated with that particular set of atoms. The partial charge reads

$$\rho^{\{s\}}(\mathbf{r})=\sum_{\mu\nu\in\{s\}}P_{\mu\nu}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\;, \tag{11}$$

where the summations are over all the orbitals of the atoms in the set $\{s\}$. The correlation energy associated with this set would then be

$$E_c^{\{s\}}=\int\left[\rho^{\{s\}}(\mathbf{r})\varepsilon_c[\rho^{\{s\}}(\mathbf{r})]-\sum_{n}^{\text{occ}}\sum_{\sigma=\uparrow,\downarrow}\rho_n^{\sigma\{s\}}(\mathbf{r})\varepsilon_c[\rho_n^{\sigma\{s\}}(\mathbf{r})]\right]d\mathbf{r}\;. \tag{12}$$

The results of the analysis of the partial correlation ener-

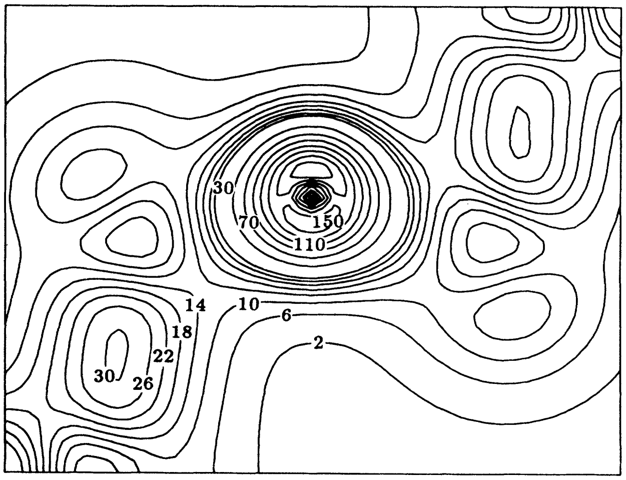

FIG. 5. Total calculated electronic charge distribution at the vicinity of interstitial oxygen in silicon. The units are electrons per bulk silicon unit cell.

gy for silicon are depicted in Fig. 4. We obtain a correlation energy per electron in the range of 0.7–0.8 eV. To study the interatomic correlation we subtract from Fig. 4(b) twice the the value of Fig. 4(a), obtaining for the nearest-neighbor correlation energy the value of -0.673 eV. With the data of Fig. 4(c) we can estimate the next-nearest-neighbor correlation energy which is negligibly small. These results clearly show the local character of the correlation energy in agreement with previous calculations performed using the local ansatz.[13,14] We can also calculate the correlation energy per silicon unit cell which gives the value of -6.812 eV as compared with -7.425 eV obtained by Ganduglia-Pirovano *et al.*[13] using the local ansatz. This is remarkable agreement considering the difference in the basis set used in the calculations and the different approaches used. Also we can calculate isolated atomic silicon which gives a correlation energy of 2.624 eV (4.816 eV total correlation and 2.192 eV self-correlation correction) as compared with the value of 2.448 eV as quoted by Ganduglia-Pirovano *et al.* The agreement of the above results stresses the appropriateness of our method of calculation and the need for the self-correlation corrections.

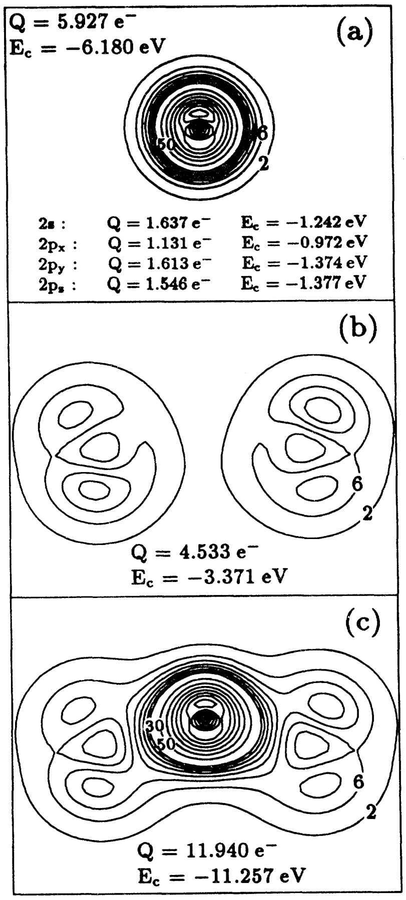

FIG. 6. Partial electronic charge distributions and the corresponding correlation energies (see the text for the definitions) near interstitial oxygen in the Si_8H_{18} cluster. (a) Oxygen atomic charge contribution. (b) Charge contributions of the two silicon atoms bonded to oxygen. (c) Charge contributions of the silicon-oxygen bond. The total charge contained in each partial distribution is indicated. The x axis is orientated along the direction joining the two silicon atoms bonded to oxygen. The units are electrons per bulk silicon unit cell.

In the same spirit we have analyzed intersitial O in silicon. The structure of the puckered Si—O—Si bond has been discussed elsewhere.[15] In Fig. 5 we show the total electronic charge near the oxygen atom. In Fig. 6 we show the correlation energy contributions of the different partial charges. We first notice that the energy correlation per electron at oxygen is about 1.04 eV which is larger than for silicon as corresponds to a higher local charge density, the correlation energy at the Si—O—Si bond being -1.958 eV in contrast with the above value of -0.673 eV of the Si—Si bond.

We can conclude this section stressing the local character of the electronic correlation in contrast with the kinetic and exchange contributions to the total energy.[16]

IV. CONCLUDING REMARKS

We have presented a method to calculate total energies in semiconductors. The method, similar to the one developed by Causa and co-workers,[3,4] entails the calculation of the Hartree-Fock energy adding, *a posteriori*, the correlation energy by means of the local-density approximation. From our analysis we can conclude the following.

(i) The method includes exactly the kinetic, Coulomb, and exchange energies for finite clusters of atoms.

(ii) The Hartree-Fock electronic charge density is in excellent agreement with the experimental charge density for crystalline silicon. This warrants the use of this charge distribution to calculate the correlation energy.

(iii) The use of finite clusters of silicon atoms suitably saturated provides a very good description of the electronic states of the infinite crystal.

(iv) In order to get a good correlation energy the self-correlation of each electron at the different molecular orbitals has to be subtracted. This is different from the self-interaction correction.[2,17] Moreover, the self-correlation discussed in this work is unambiguously defined.

(v) The method of calculation allows us to show in a simple manner the local character of the correlation energy in contrast to the kinetic and exchange energies.[16]

(vi) The method as it stands is not fully self-consistent, with only the Hartree-Fock part being done self-consistently. Its extension to a fully self-consistent procedure is conceptually simple and will be considered in the future.

(vii) The method only allows us to study ground-state properties; however, quasiparticle energies can be calculated if a proper self-energy operator is included.[9]

(viii) The extension of the method to study open-shell problems is possible and is under consideration.

ACKNOWLEDGMENTS

We would like to acknowledge A. Lizón for his help during the early stages of this work and O. Gunnarsson for a critical reading of the manuscript. Also we would like to thank the Max Planck Institute where part of this work was done. One of us (F. Y.) gratefully acknowledges support from the Alexander von Humboldt Stiftung. This work has been partially supported by the CICyT.

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