Exchange Correlation Energy as a Function of the Orbital Occupancies: Implementation on First Principles Local Orbital Methods

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ABSTRACT: We introduce a local density formalism, where the total energy of the system is obtained as a function of the orbital occupancies $\{n_{\mu\sigma}\}$. The exchange energy, E^X is written in terms of the electrostatic interaction between a charge $n_{\mu\sigma}$ and its hole $(1 - n_{\mu\sigma})$, while the correlation energy is analyzed by means of a Hubbard Hamiltonian using a dynamic field approximation. Once the exchange correlation energy is obtained as an explicit function of the $\{n_{\mu\sigma}\}$, our orbital occupancy method is completely defined. Our approach is then applied to bulk diamond, Si, and zinc-blende GaN, as well as the benzene molecule. The results obtained show that this approach offers an interesting alternative to the well-established density functional theory methods based on the electron density $\rho(\vec{r})$. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 91: 151–156, 2003

Key words: density functional theory; orbital occupancy; exchange correlation function; Hubbard Hamiltonian; many-body calculations

1. Introduction

Many modern approaches to first-principles calculations of total energy and electronic structure are based on density functional theory (DFT), which employs the electronic density as the fundamental quantity. However, the exact exchange-correlation energy functional is not known and an appropriate approximation becomes essential. At the same time, highly correlated electron systems are often studied by solving model Hamiltonians, such as the Anderson, Hubbard, or generalized Hubbard. The orbital occupancy (OO) method [1] presented in this article combines the natural advantages of these two approaches by expressing the energy and potentials in terms of the orbital occupancies $\{n_{\mu\sigma}\}$. These $\{n_{\mu\sigma}\}$ are the inher-

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ent variables of generalized Hubbard Hamiltonians, from which our exchange-correlation energies are derived.

The OO method thus provides a formalism that allows us to include in a natural way the many-body corrections while maintaining the calculational simplicity on the local density approximation (LDA) level. This method is based on an alternative approach to DFT, in which instead of the electronic density $\rho(\vec{r})$ we use the orbital occupancies $\{n_{\mu\sigma}\}$ as the central quantity:

$$\rho(\vec{r}) \Rightarrow \{n_{\mu\sigma}\}. \tag{1}$$

The usual DFT is based on the Hohenberg–Kohn theorem [2]. This theorem can be rewritten in terms of $\{n_{\mu\sigma}\}$ (see Ref. [1]), showing that the total energy is a function of the orbital occupancies, $E = E[\{n_{\mu\sigma}\}]$, and the energy of the ground state is found at the minimum of the function.

In a similar way as the Kohn–Sham equations in the ρ-based DFT, we introduce an effective Hamiltonian $\hat{H}_{\text{eff}}$ using

$$V_{\mu\sigma} = \frac{\partial E[\{n_{\nu\sigma}\}]}{\partial n_{\mu\sigma}}. \tag{2}$$

Thus, the $\{n_{\mu\sigma}\}$ can be determined self-consistently via $\hat{H}_{\text{eff}}$ eigenfunctions $|\varphi_{\alpha\sigma}\rangle$ (where σ means spin) as

$$n_{\mu\sigma} = \sum_{\alpha=\text{occ.}} |\langle\phi_\mu|\varphi_{\alpha\sigma}\rangle|^2. \tag{3}$$

because $\hat{H}_{\text{eff}}$, in turn, depends on the $\{n_{\mu\sigma}\}$. The functions $\{\phi_\mu\}$ are Löwdin orthonormal orbitals, which are obtained from nonorthogonal atomic-like orbitals $\{\psi_\nu\}$, optimized for each system:

$$\phi_\mu = \sum_\nu (S^{-1/2})_{\mu\nu}\psi_\nu, \tag{4}$$

where $S_{\mu\nu}$ is the overlap matrix $\langle\psi_\mu|\psi_\nu\rangle$.

The Hartree part of the energy is calculated using a self-consistent Harris-like approach [3, 4], a method applied with success in many calculations (see, e.g., [5] and references therein).

In similarity with the standard DFT, it is not possible in general to find an analytic expression for the exact exchange correlation energy $E^{\text{XC}}[\{n_{\nu\sigma}\}]$. In Section 2, $E^{\text{XC}}[\{n_{\nu\sigma}\}]$ is analyzed using a generalized Hubbard Hamiltonian and many-body techniques. This approach facilitates the description of electron-correlated effects improving on the LDA or generalized gradient approximation (GGA). Moreover, the OO formalism can be used as a starting point for the many-body calculations needed to properly describe strongly correlated systems [6]. In Section 3, we show the performance of this approach, presenting some results for bulk C, Si, and zinc-blende GaN, as well as the benzene molecule.

2. Exchange Correlation Energy

In this section we will define the exchange correlation energy function $E^{\text{XC}}[\{n_{\nu\sigma}\}]$ and the effective potential $V^{\text{XC}}[\{n_{\nu\sigma}\}]$. The most important contributions to exchange and correlation come from the Coulomb interactions U_ν and $J_{\mu\nu}$, so we can elicit the dependence E^{XC} on $\{n_{\nu\sigma}\}$ with the help of a generalized Hubbard Hamiltonian, written as

$$\hat{H}^{\text{GH}} = \sum_{\nu\sigma} E_{\nu\sigma}\hat{n}_{\nu\sigma} + \sum_{(\nu,\mu),\sigma} T^{\sigma}_{\nu\mu}\hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\mu\sigma} + \frac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma,\sigma'} J_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma'} + \sum_\nu U_\nu\hat{n}_{\nu\downarrow}\hat{n}_{\nu\uparrow}, \tag{5}$$

where

$$U_\nu = \int \phi^2_\nu(\vec{r})\,\frac{1}{|\vec{r}-\vec{r}\,'|}\,\phi^2_\nu(\vec{r}\,')d\vec{r}d\vec{r}\,', \qquad J_{\nu\mu} = \int \phi^2_\nu(\vec{r})\,\frac{1}{|\vec{r}-\vec{r}\,'|}\,\phi^2_\mu(\vec{r}\,')d\vec{r}d\vec{r}\,'. \tag{6}$$

In the calculation of E^{XC} for real systems it is necessary to include terms that do not appear explicitly in the Hamiltonian (5). We calculate the exchange energy contributions of these terms in the mean field approximation. In practice, we have found that we can neglect all but two-center, nearest-neighbor interactions (see Ref. [6] for further discussion). An important example of the terms we retain is

$$-\frac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma} J^x_{\nu\mu} n_{\nu\sigma} n_{\mu\sigma}, \tag{7}$$

where $J^x_{\nu\mu}$ is the exchange interaction given by

$$J^x_{\nu\mu} = \int \phi_\nu(\vec{r})\phi_\mu(\vec{r})\,\frac{1}{|\vec{r}-\vec{r}'|}\,\phi_\nu(\vec{r}')\phi_\mu(\vec{r}')d\vec{r}d\vec{r}' \quad (8)$$

and is included in the effective Hamiltonian as $V^{J^x}_{\mu\sigma} = -\sum_\nu J^x_{\nu\mu} n_{\mu\sigma}$. This term is necessary to ensure that the first Hund rule is observed.

2.1. GENERALIZED HUBBARD HAMILTONIAN

The exchange correlation energy of (5) is partitioned as follows:

$$E^{\mathrm{XC}} = E^{\mathrm{SIC}} + E^X + E^{C,I}. \quad (9)$$

The first term is the self-interaction correction (SIC):

$$E^{\mathrm{SIC}} = -\frac{1}{2}\sum_{\mu\sigma} U_\mu n_{\mu\sigma} n_{\mu\sigma} \rightarrow V^{\mathrm{SIC}}_{\mu\sigma} = -U_\mu n_{\mu\sigma}, \quad (10)$$

which cancels exactly the intra-atomic Hartree contribution; for this reason, it does not appear in (5). Thus, we can see that the OO method, unlike LDA and GGA, treats correctly this contribution. The second term is the exchange energy due to the Coulomb interaction J. The dependence of E^X on diagonal occupancies can be written as [1]

$$E^X = -\frac{1}{2}\sum_{\mu\sigma} J_\mu n_{\mu\sigma}(1-n_{\mu\sigma}). \quad (11)$$

This formula can be interpreted as a contribution to the total energy coming from the interaction of the charge $n_{\mu\sigma}$ with its exchange hole $(1-n_{\mu\sigma})$ [6]. J_μ is well approximated by the mean Coulomb interaction between electrons on nearest-neighbor atoms J^{NN}_μ. This is exact in the dynamic mean field (DMF) approximation [8], where all the exchange hole is localized on nearest-neighbor atoms and no extra-atomic correlation energy appears.

According to formula (2), the effective potential associated with E^X is

$$V^X_{\mu\sigma} = -J^{\mathrm{NN}}_\mu\left(\frac{1}{2} - n_{\mu\sigma}\right). \quad (12)$$

The last term on the right side of Eq. (9) is the intra-atomic correlation energy. We consider this the most important contribution to the electronic correlation. Intra-atomic correlation effects appear when part of the exchange correlation hole, which should integrate to $1-n_{\mu\sigma}$, is transferred to the same atom of the $\mu\sigma$-orbital. If a fraction, say $f_{\mu\sigma}$ $(f_{\mu\sigma} < 1)$, of this hole is located in the atom, the intra-atomic correlation energy should be given by $-(f_{\mu\sigma}/2)\langle U_\mu\rangle n_{\mu\sigma}(1-n_{\mu\sigma})$, while the exchange and interatomic correlation energy is reduced to $-1/2\,(1-\mathrm{f}_{\mu\sigma})\mathrm{J}^{\mathrm{NN}}_\mu n_{\mu\sigma}(1-n_{\mu\sigma})$. Then, both contributions, $E^X + E^{C,I}$, yield [6]

$$-\frac{1}{2}\sum_{\mu\sigma} J^{\mathrm{NN}}_\mu n_{\mu\sigma}(1-n_{\mu\sigma}) - \frac{1}{2}\sum_{\mu\sigma} f_{\mu\sigma}(\langle U_\mu\rangle - J^{\mathrm{NN}}_\mu) n_{\mu\sigma}(1-n_{\mu\sigma}), \quad (13)$$

where $\langle U_\mu\rangle$ is an average of the intra-atomic Coulomb interactions.

The above argument suggests that we can consider intra-atomic correlation effects by studying a Hubbard Hamiltonian with an effective interaction in an atomic site i given by $\tilde{U}_i = \langle U_\mu\rangle - J^{\mathrm{NN}}_\mu$. This will be the subject of Section 2.2.

2.2. HUBBARD HAMILTONIAN

The Hubbard Hamiltonian, better known in the chemistry community as the Pariser–Parr–Pople Hamiltonian [7], we will use here is

$$\hat{H}^H = \sum_{\nu\sigma} \tilde{E}_{\nu\sigma}\hat{n}_{\nu\sigma} + \sum_{(\nu,\mu),\sigma} T^\sigma_{\nu\mu}(\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma}) + \frac{1}{2}\sum_{\substack{\mu\sigma',\nu\sigma\neq\mu\sigma' \\ (\mu,\nu\in i)}} \tilde{U}_i \hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma'}. \quad (14)$$

The correlation energy of this Hamiltonian is obtained as an interpolation between two limits where it can be properly approximated [6]. They are the atomic limit $\tilde{U}/T \rightarrow \infty$ and the $\tilde{U}/T \rightarrow 0$ limit, where we can apply second-order perturbation theory.

2.2.1. Atomic Limit $\tilde{U}/T \rightarrow \infty$

In this limit we have calculated the correlation energy using Green functions' techniques. We will present here only the final expression; a detailed derivation can be found in Section III of Ref. [6]:

$$E^{C,I} = -\frac{1}{2}\sum_{\mu\sigma}\tilde{U}_i n_{\mu\sigma}(1-n_{\mu\sigma}) + \frac{1}{2}\tilde{U}_i(\mathcal{N}_i - N_i)(1+N_i-\mathcal{N}_i), \quad (15)$$

with $\mathcal{N}_i = \Sigma_{\mu\sigma} n_{\mu\sigma}$ and $N_i = \mathrm{Int}[\mathcal{N}_i]$. The first term in this equation is associated with fluctuations of charge in each orbital and the second with total atomic charge fluctuations.

2.2.2. Second-Order Perturbation Theory $\tilde{U}/T \to 0$

Here we approximate the correlation energy as

$$E^{C,I} = -\frac{1}{2}\sum_{\substack{\nu\sigma',\mu\sigma\neq\nu\sigma' \\ (\mu,\nu\in i)}} \tilde{U}_i^2 \frac{n_{\mu\sigma}(1-n_{\mu\sigma})n_{\nu\sigma'}(1-n_{\nu\sigma'})}{W_{\mu\sigma;\mu\sigma}+W_{\nu\sigma';\nu\sigma'}} - \frac{1}{2}\sum_{\substack{\nu\sigma',\nu\sigma\neq\nu\sigma' \\ \alpha\sigma,\beta\sigma'\neq\alpha\sigma \\ (\mu,\nu\in i) \\ (\alpha,\beta\in j\neq i)}} \tilde{U}_i\tilde{U}_j \frac{n^2_{\mu\sigma;\alpha\sigma}n^2_{\nu\sigma';\beta\sigma'}}{W_{\mu\sigma;\alpha\sigma}+W_{\nu\sigma';\beta\sigma'}}, \quad (16)$$

where $W_{\mu\sigma;\alpha\sigma}$ is the mean virtual excitation energy related to the density of states $\rho_{\mu\sigma;\alpha\sigma}(\omega)$. The first term represents virtual excitations of two electrons in the same atom. The second represents excitations of two electrons in nearest-neighbor atoms, this term being inversely proportional to the coordination number. Thus, it must be included for the study of few-atom systems, and it disappears in the DMF approximation.

2.2.3. Interpolation Between the Limits

Now we define the correlation energy function as an interpolation between the above two limits [6]. In the systems we study, the second term in (15) is negligible because it becomes important only near the atomic limit. Therefore, we consider the following correlation energy function:

$$E^{C,I} = -\frac{1}{2}\sum_{\mu\sigma} f(x_{\mu\sigma})\tilde{U}_i n_{\mu\sigma}(1-n_{\mu\sigma}), \quad (17)$$

where

$$x_{\mu\sigma} = \sum_{\substack{\nu\sigma'\neq\mu\sigma \\ (\mu,\nu\in i)}} \frac{\tilde{U}_i n_{\nu\sigma'}(1-n_{\nu\sigma'})}{W_{\mu\sigma;\mu\sigma}+W_{\nu\sigma';\nu\sigma'}} + \sum_{\substack{\nu\sigma'\neq\mu\sigma \\ \beta\sigma',\alpha\sigma\neq\beta\sigma' \\ (\mu,\nu\in i) \\ (\alpha,\beta\in j\neq i)}} \frac{\tilde{U}_j}{W_{\mu\sigma;\alpha\sigma}+W_{\nu\sigma';\beta\sigma'}} \frac{n^2_{\mu\sigma;\alpha\sigma}n^2_{\nu\sigma';\beta\sigma'}}{n_{\mu\sigma}(1-n_{\mu\sigma})}. \quad (18)$$

To assure the correct limits of $E^{C,I}$, f must have the following asymptotic behavior: $f(x) \to x$ for $x \to 0$ and $f(x) \to 1$ for $x \to \infty$. The $f(x)$ was fitted to obtain the correct correlation energy in small clusters. The exchange correlation energy function and its associated potential is now completely defined.

Finally, we stress that, following the same ideas discussed in this section, a many-body solution can also be obtained [6]. In this case we use Green function techniques and introduce diagonal self-energies $\Sigma^{\sigma}_{i\alpha\alpha}(\omega)$. This implies neglecting off-diagonal contributions, as corresponds to the DMF approximation [8]. As in the case of the intra-atomic correlation energy, the calculation of the self-energy is based on an interpolative approach between the high and low correlation limits. It can be shown [6] that the effective one-particle solution of the many-body problem is given by the OO approach presented above. The knowledge of the correlation potential in our method allows us to avoid the double-counting problem occurring in the many-body calculations, which start from the standard DFT solutions.

3. Results

In this section we present results obtained with the OO method described above. For the sake of brevity we do not include results of many-body calculations, which will be published elsewhere. To test the OO method we calculated structural parameters and band structures of diamond and silicon with a minimal basis set consisting of Fireball orbitals [3]. In the calculation of the correlation energy we take into account the relaxation of the orbitals due to local charge fluctuations. The accuracy of the structural parameters obtained with OO is comparable to typical LDA results with the same minimal basis: lattice parameters for Si are 5.437 (OO) and 5.425 (LDA) compared to experimental 5.429 Å, while for C they are 3.61 (OO) and 3.62 (LDA) compared to 3.567 Å. The calculated electronic band gaps seem to present a correction to the "band

gap problem" [9] of the LDA and GGA. For diamond the OO band gap at Γ is $E_g^{OO} = 6.5$ eV as compared to the experimental values $E_g^{exp} = 7.3$ eV and to LDA's $E_g^{LDA} = 5.6$ eV [10]. For silicon the results for the indirect gap were: $E_g^{OO} = 1.6$ eV, $E_g^{exp} = 1.2$ eV, and E_g^{LDA} ($\Gamma - X$ gap) = 0.6 eV. In the next subsections we present out results for zinc-blend GaN and the benzene molecule.

3.1. SELF-INTERACTION CORRECTIONS IN THE *Ga*-3*d* BANDS OF GaN

LDA or GGA plane-wave calculations for GaN show the need to include the *core Ga*-3*d* states explicitly in the calculations to obtain the lattice parameter correctly. When this is done, the *Ga*-3*d* bands appear as overlapping the *N*-2*s* bands, in contradiction with the experimental evidence, which shows the *Ga*-3*d* states well below the *N*-2*s* bands. This discrepancy is due to the localized character of the *Ga*-3*d* states. The imperfect cancellation of Hartree contributions by the XC terms in the standard LDA or GGA functionals pushes up the electronic levels, and the proper description of these levels requires the use of self-interaction corrections [11]. Our method provides a good description of the structural properties of GaN (comparable to that of the standard functionals with the same basis) and corrects the problem in the description of the localized states. In the band structure shown in Figure 1, the *Ga*-3*d* states appear several electron volts below the *N*-2*s* bands, in good agreement with the experiment. Notice that in the OO-method a self-interaction correction term appears naturally [see Eq. (10)].

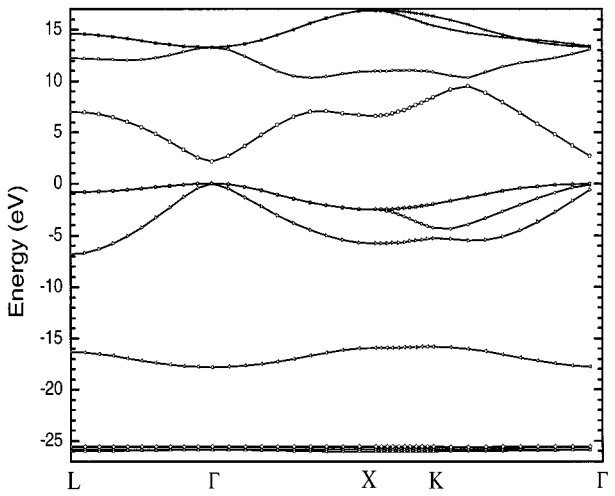

FIGURE 1. Band structure for GaN calculated within the OO approach. This method includes self-interaction corrections, which provide a good description of the *Ga*-3*d* bands.

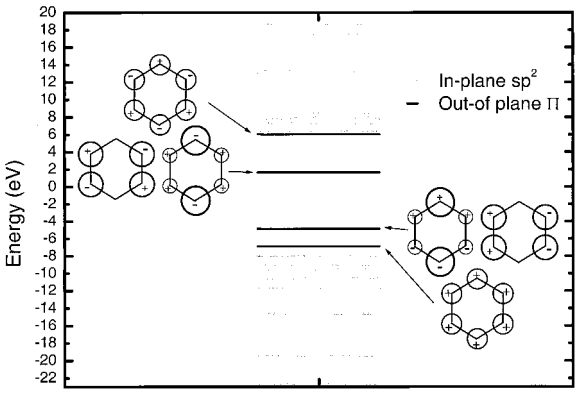

FIGURE 2. OO one-particle spectrum for the molecular orbitals of benzene. The calculated HOMO-LUMO gap is 6.5 eV.

3.2. BENZENE MOLECULE

The OO method has been used to calculate the electronic properties of the benzene molecule. A double-zeta minimal basis set from Clementi and Roetti [12] was variationally optimized for benzene. The bond lengths at the equilibrium geometry are in reasonable agreement with experiment (OO: CC, 1.47 Å; CH, 1.15 Å; Exp. [13]: CC, 1.40 Å; CH, 1.10 Å). In our calculations we included intra-atomic exchange and found a significant contribution of the second term of Eq. (16) to the correlation energy.

For the binding (E^b) we obtain: $E^b = -45.6$ eV to be compared with $E^b_{exp} = -59.7$ eV [14]. From Hartree–Fock calculations [14] we find that this difference comes from the minimal basis used in the calculation, 9.0 eV, and from an underestimation of the many-body energy, 5.1 eV. This error should be compared with the total many-body energy of the molecule that we find around 310 eV. Figure 2 shows the single-particle spectrum corresponding to the molecular orbitals of the effective one-particle Hamiltonian. The HOMO and LUMO are doubly degenerate Π states, and our calculated HOMO–LUMO gap is 6.5 eV, compared to the mean experimental excitation energy $e_{1g} \rightarrow e_{2u}$ of 6.2 eV [15]. This is a satisfactory result considering that this is a neutral excitation.* These results for ben-

*More details about our calculated energy gaps and the experimental optical gaps will be published elsewhere.

zene illustrate the accuracy of our method and the quality of our many-body treatment for molecules.

4. Summary

In this article we have presented a DFT-like approach based on the orbital occupancies $\{n_{\mu\sigma}\}$ [instead of the electron density $\rho(\vec{r})$] [6]. The exchange correlation energy E^{XC} has been determined as a function of $\{n_{\mu\sigma}\}$ with the help of a generalized Hubbard Hamiltonian that contains the most important contributions to the electron–electron energy. The intra-atomic correlation energy is obtained as an interpolation between the corresponding high and low correlation limits. We have pointed out that, within the same approximations, a many-body solution can also be obtained, replacing the correlation potential by the corresponding self-energy. We also presented some calculations for molecules and crystals using a minimal basis set and neglecting all but the two-center nearest-neighbors exchange integrals, although these approximations are not essential to the OO method and can be dropped in a more accurate calculation. The numerical results presented in Section 3 show that this approach offers an interesting alternative to the well-established DFT methods based on the electron density $\rho(\vec{r})$, especially for systems that present significant electron correlation effects.

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References

1. García-Vidal, F. J. et al. Phys Rev B 1994, 50, 10537.
2. Hohenberg, P.; Kohn, W. Phys Rev B 1964, 136, 864.
3. Demkov, A. A. et al. Phys Rev B 1995, 52, 1618.
4. Ortega, J. Comput Mater Sci 1998, 12, 192.
5. Lewis, J. P. et al. Phys Rev B 2001, 64, 195103.
6. Pou, P. et al. Phys Rev B 2000, 62, 4309.
7. Parr, R. Quantum Theory of Molecular Electronic Structure; Benjamin: New York, 1964.
8. Georges, A.; Kotliar, G.; Krauth, W.; Rozenberg, M. J. Rev Mod Phys 1996, 68, 13.
9. Kunz, A. B. Phys Rev B 1972, 6, 606.
10. Städele, M. et al. Phys Rev B 1999, 59, 10031.
11. Vogel, D. et al. Phys Rev B 1996, 55, 12836.
12. Clementi, E.; Roetti, C. Atom Nucl Data Tables 1974, 14, 177.
13. Lide, D. R., ed. Handbook of Chemistry and Physics, 79th Ed.; CRC Press: Boca Raton, FL, 1998.
14. Clementi, E. In: Modern Techniques in Computational Chemistry: MOTECC-909; ES-COM: Leiden, 1990, 383.
15. Baldo, M. et al. Chem Phys Lett 1981, 83, 309.