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1998 J. Phys.: Condens. Matter 10 8257

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Self-consistent tight-binding formalism for charged systems

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Received 25 March 1998, in final form 3 June 1998

Abstract. Tight-binding (TB) methods are designed to work for neutral systems. When an electron is added to or subtracted from the system, or when an external field is applied to the system, one should handle the problem of screening and charge redistribution in a self-consistent manner. Here, we have proposed a simple way to calculate the potential due to an external field and the corrected Hartree potential. A straightforward way to compute the Coulomb (Hubbard) integrals for any atom is also demonstrated. This formalism has been tested against *ab initio* calculations for carbon C_{20} and silicon Si_{12} clusters. Good agreement between *ab initio* and self-consistent TB results is found.

1. Introduction

Due to the computing limitation of first-principles density functional (DF) methods, many researchers use the tight-binding (TB) method to calculate electronic and mechanical properties of materials, and more specifically large clusters such as fullerenes. Unlike in *ab initio* methods, the tight-binding Hamiltonian is ‘blind’ as regards the charge of the system. In other words, it predicts the same eigenvalues and eigenvectors for a system of any charge. The only difference between these systems is their occupation number, which would yield different total energies and forces. But adding an electron to the system changes the Hamiltonian by adding a repulsive Coulomb interaction between the electrons; as a result, the electronic eigenvalues will be shifted upwards. Furthermore, for a charge-neutral system, the TB method is unable to properly take into account the screening of an external field. On the other hand, it is well known that the shortcoming of the TB method is its not-so-good transferability even if one uses a non-orthogonal basis. Indeed, the response of the electrons would be different to the field created by different atomic environments. The electron density on a given atom could be low or high depending on the amount of charge transfer; this in turn would affect the potential via Poisson’s equation, and therefore the Hamiltonian matrix elements. In some of the literature, this is called the charge-transfer effect, and, to overcome this, an *ad hoc* Hubbard-like term is usually added to the Hamiltonian [1–3]. This requires a self-consistent solution of the problem, since the Hubbard term is linear in the change in the charge density, which itself depends on the eigenfunctions of the Hamiltonian. The Hubbard coefficient U is usually determined empirically by a fitting to the *ab initio* data for the dimer or other structures with different environments, for example. The addition of such a term is in fact crucial in ensuring good transferability of a given parametrization even if it is a non-orthogonal one. It is the purpose of this paper to include such effects, in a more quantitative way, into the tight-binding formalism in order to circumvent all of the problems mentioned above.

In what follows, the physical origin of this term will be established by looking at the effect of the addition of a charge, and we will show how the Hubbard parameters can be found. Finally, the results of this treatment will be illustrated by considering a few examples: the TB results for charged systems will be compared to *ab initio* calculations for C_{20} corranulene, and icosahedral Si_{12} .

2. Theory

Let us consider the Hamiltonian of a finite system in the neutral configuration, and denote it by H_0 . The addition of an electron will add an electrostatic Coulomb term and an exchange–correlation (XC) term to it. (Here we are considering a one-electron Hamiltonian, and therefore use the appropriate language for describing the Coulomb interaction.) In the mean-field or first-order perturbation theory, one considers the average of the perturbation in an eigenstate to obtain the shift in the corresponding eigenvalue. This first-order shift can be interpreted as the electrostatic interaction between the added electron and the electronic charge distribution of the eigenstate considered. The change in the exchange–correlation potential is neglected.

After expanding this eigenstate in the TB basis functions:

$$|\psi_\lambda\rangle = \sum_{i\alpha} C_{i\alpha}^\lambda |\phi_{i\alpha}\rangle$$

one finds, for a negatively charged system for example, the following expression for the shift in the eigenvalues due to the electrostatic field of the added charge $\delta\rho$:

$$\varepsilon_\lambda - \varepsilon_\lambda^0 = \langle \psi_\lambda | \delta H | \psi_\lambda \rangle = \langle \psi_\lambda(r) | \int \frac{\delta\rho(r')}{|r-r'|} dr' | \psi_\lambda(r) \rangle \quad (1)$$

$$= \int \frac{\rho_\lambda(r) \delta\rho(r')}{|r-r'|} dr dr' \quad (2)$$

$$= \sum_{i\alpha, j\beta, k\gamma, l\delta} C_{i\alpha}^{\lambda*} C_{j\beta}^\lambda C_{k\gamma}^{N+1*} C_{l\delta}^{N+1} U_{ij,kl}^{\alpha\beta, \gamma\delta}. \quad (3)$$

The added charge ($\delta\rho$) will fill the lowest unoccupied molecular orbital (LUMO), denoted here as orbital $N+1$. The Coulomb integral U is defined as

$$U_{ij,kl}^{\alpha\beta, \gamma\delta} = \int \phi_{i\alpha}^*(r) \phi_{j\beta}(r) \frac{1}{|r-r'|} \phi_{k\gamma}^*(r') \phi_{l\delta}(r') dr dr'. \quad (4)$$

The orbitals ϕ are assumed to be real; the Roman indices i, j, k, l refer to atomic sites, and the Greek indices to their orbitals. The parameter U , usually referred to as the Hubbard parameter for historical reasons, represents the Coulomb interaction kernel $1/|r-r'|$, but it is represented by a tensor $U_{ij,kl}^{\alpha\beta, \gamma\delta}$ once a basis is adopted for representing the Hamiltonian and the charge density.

The added charge will affect the ground-state charge distribution itself, and, therefore, instead of considering first-order perturbation theory, one can calculate the matrix elements of the new perturbed Hamiltonian, and diagonalize it numerically and self-consistently to obtain the exact shift of the eigenvalues. This approach, allowing for the relaxation of the ground-state charge density, will partially include correlation effects as well.

When expanding wavefunctions and densities in a basis (localized in this case), all ground-state properties of the system can be written as a function of the density matrix, defined by

$$Q_{ij}^{\alpha\beta} = \sum_\lambda n_\lambda C_{i\alpha}^{\lambda*} C_{j\beta}^\lambda. \quad (5)$$

The sum over λ is over the eigenstates with occupation $n_\lambda = 2$ (spin) for occupied states and 0 for empty states. By using the density matrix, the change in the Hamiltonian operator H and that in its matrix \mathcal{H} can be written, respectively, as follows:

$$\delta H(r) = \int \frac{\delta \rho(r')}{|r - r'|} dr' \quad (6)$$

$$\delta \mathcal{H}_{ij}^{\alpha\beta} = \sum_{kl, \gamma\delta} U_{ij,kl}^{\alpha\beta, \gamma\delta} (\rho_{kl}^{\gamma\delta} - \rho_{kl}^{0\gamma\delta}). \quad (7)$$

Here, the superscript 0 refers to the neutral unperturbed ground state. It can be seen from the above equation that the matrix element is a product of two terms: one is the two-particle Coulomb integral, and the other factor is the change in the density matrix $\rho_{ij}^{\alpha\beta}$. If the latter is diagonal, one recovers the often-used Hubbard term $U(n_i - n_i^0)$, which is the correction to the Hartree potential, i.e. it represents the electrostatic Coulomb potential of the induced (or added) charge. The additional Coulomb interaction was the reason for which, physically, the above term needed to be added to H_0 . One can also see this mathematically, as the matrix elements of H_0 were defined from a fit to crystalline band structures where there is no charge transfer. Therefore, for a surface or a cluster, or a charged system, there must be a correction to these matrix elements. To first order, this correction is linear in the charge difference $\delta\rho$, and U can be seen as the proportionality constant in this expansion, which, according to Taylor's formula, should be the first derivative of the Hamiltonian with respect to the charge density:

$$H(\rho) = H(\rho_0) + \mathcal{U} \delta\rho + \mathcal{O}(\delta\rho^2).$$

Within the DF formalism, \mathcal{U} is given by

$$\mathcal{U}_{ij,kl}^{\text{DF}} = \int \phi_i^*(r) \phi_j(r) \left(\frac{\partial v_{xc}(r)}{\partial \rho(r')} + \frac{1}{|r - r'|} \right) \phi_k^*(r') \phi_l(r') d^3r d^3r' \quad (8)$$

and, in Hartree–Fock (HF) theory, it is defined as

$$\mathcal{U}_{ij,kl}^{\text{HF}} = \int \frac{\phi_i^*(r) \phi_j(r) \phi_k^*(r') \phi_l(r') - \frac{1}{2} \phi_i^*(r) \phi_j(r') \phi_k^*(r') \phi_l(r)}{|r - r'|} d^3r d^3r' = U_{ij,kl} - \frac{1}{2} U_{il,kj}. \quad (9)$$

Here the Greek superscripts have been dropped, but i, j, k, l can be thought of as basis indices. Notice that we have still reserved U for the pure electrostatic Coulomb term (equation (4)), and the term indicated in calligraphic font, \mathcal{U} , includes the exchange–correlation effects.

One can discuss the effect of exchange in a linear combination of atomic orbitals (LCAO) HF formalism. Because of the small overlap, the exchange contribution is usually very small, except when the four orbitals are localized on the same atom. The exchange, therefore, appears only in the on-site terms of U through $U^{\alpha\beta, \alpha\beta} \delta \rho^{\beta\beta}$, and should be included if $U^{\alpha\beta, \alpha\beta}$ is large. In general, its effect becomes important when the off-diagonal terms of the density matrix are large. Such is the case for metallic systems, where the density matrix is long ranged; in this case too, this term must be included.

The other concept for which this treatment is relevant is that of the chemical hardness [4]. It is defined as

$$\eta_{\lambda\mu} = \frac{\partial^2 E}{\partial n_\lambda \partial n_\mu} \quad (10)$$

where n_λ and n_μ are the occupation numbers of the eigenstates λ and μ . The first derivative is of course the single-particle eigenvalue ε_λ , and the second tells us how this eigenvalue

changes as the occupation number of another level μ is changed. This is exactly the shift of the eigenvalues as the system is charged (e.g. $\eta_{\lambda,N+1}$). In other words, we had calculated in equation (3) the chemical hardness by taking the state μ as being the lowest unoccupied state, and λ as any other state. The chemical hardness matrix allows one to predict the effect of any charge transfer (or, more generally, any change in the occupation numbers) on the eigenvalues of the system. It is related to \mathcal{U} by

$$\eta_{\lambda,\mu} = \sum_{i\alpha,j\beta,k\gamma,l\delta} C_{i\alpha}^{\lambda*} C_{j\beta}^{\lambda} C_{k\gamma}^{\mu*} C_{l\delta}^{\mu} \mathcal{U}_{ij,kl}^{\alpha\beta,\gamma\delta} \quad (11)$$

and the shifts in the energy levels are given by

$$\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + \sum_{\mu} \eta_{\lambda,\mu} (n_{\mu} - n_{\mu}^0). \quad (12)$$

As one can see, η involves the eigenstates of the system, and therefore depends on the specific system considered, although its atomic value has also been used in some of the literature [5] in order to compute the charge transfer in neutral systems.

Appropriate screening of an external field can also be treated by this method. If one approximates the matrix elements of the external field as follows:

$$\langle i\alpha | V | j\beta \rangle = \int \phi_{i\alpha}^*(r) V(r) \phi_{j\beta}(r) dr \approx \frac{1}{2} S_{ij}^{\alpha\beta} (V(R_i) + V(R_j)) \quad (13)$$

where $S_{ij}^{\alpha\beta}$ is the overlap matrix, the matrix elements of the perturbed Hamiltonian can easily be calculated:

$$\langle i\alpha | \delta H | j\beta \rangle = \langle i\alpha | V | j\beta \rangle + \sum_{kl,\gamma\delta} \mathcal{U}_{ij,kl}^{\alpha\beta,\gamma\delta} (\varrho_{kl}^{\gamma\delta} - \varrho_{kl}^{0\gamma\delta}). \quad (14)$$

The second term, the induced potential, which is the change of H due to the change in the charge density, involves the full Coulomb term $\mathcal{U} = \partial H / \partial \rho$, and not just the electrostatic induced potential defined with U .

In usual TB formalisms, the total energy of the unperturbed system is a sum of a band term (the sum of the occupied eigenvalues) and an empirical repulsive potential. This potential substitutes for the residual terms in the total energy:

$$E_{rep}(R_1, \dots, R_N) = V_{ion-ion} - \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho] - \int v_{xc}[\rho](r)\rho(r) dr. \quad (15)$$

When an electron is added to the system, this repulsive energy is modified due to the change in the charge density ρ . Using the above definition of E_{rep} , one can write the total energy within this formalism as

$$E[\rho, R] = \text{Tr } \rho \mathcal{H} + E_{rep}[R] - \frac{1}{2} \int \frac{\rho(r)\rho(r') - \rho^0(r)\rho^0(r')}{|r-r'|} dr dr' + \delta(\text{XC corrections}). \quad (16)$$

The first term, i.e. the sum of the eigenvalues of the perturbed system, includes the effect of an external potential as well. The last two terms are necessary since they represent the change in the Coulomb energy due to charging effects. Written in the TB basis, and using the symmetry of the kernel \mathcal{U} under exchange of ij and kl , it can be expressed as

$$\Delta E_{\text{Coulomb}} = \frac{1}{2} \sum_{i\alpha,j\beta,k\gamma,l\delta} \delta \varrho_{ij}^{\alpha\beta} \Sigma \varrho_{kl}^{\gamma\delta} \mathcal{U}_{ij,kl}^{\alpha\beta,\gamma\delta} \quad (17)$$

where $\delta\rho = \rho - \rho^0$ and $\Sigma\rho = \rho + \rho^0$. It must be noted that this correction also includes corrections to the exchange–correlation energy, since we have used \mathcal{U} and not the electrostatic quantity U . The final expression for the total energy then reads

$$E[\rho, R] = \text{Tr } \rho \mathcal{H}^0 + \frac{1}{2} \delta\rho \mathcal{U} \delta\rho + E_{rep}[R]. \quad (18)$$

As an example, by using this formalism, we have treated the electronic structure of a nanotube doped with donor and acceptor atoms modelled by point charges [6]. In usual treatments, one just shifts up the Fermi level in order to take the effect of charge transfer into account. The electrostatic field of the point charges is, however, neglected. We have shown that including the impurities yields a result different from that obtained by the usual treatment, especially as regards charge distribution.

3. Calculation of the Coulomb integral \mathcal{U}

As we can see from equations (8) and (9), the integral \mathcal{U} involves four atoms i, j, k, l with four orbitals; it depends on the choice of the basis functions and not on the electronic structure of the system considered (in the DF case, however, it would slightly depend on the whole system as well, but we neglect this dependence). This integral will be small if $i \neq j$ or $k \neq l$ since the overlap is then small. It has its largest value when $i = j = k = l$; we call this type of term an on-site term. We may further approximate the other terms in general by

$$\mathcal{U}_{ij,kl}^{\alpha\beta,\gamma\delta} \simeq \frac{1}{4} S_{ij}^{\alpha\beta} S_{kl}^{\gamma\delta} (\mathcal{U}_{ii,kk}^{\alpha\alpha,\gamma\gamma} + \mathcal{U}_{jj,kk}^{\beta\beta,\gamma\gamma} + \mathcal{U}_{ii,ll}^{\alpha\alpha,\delta\delta} + \mathcal{U}_{jj,ll}^{\beta\beta,\delta\delta}). \quad (19)$$

For $\mathcal{U}_{ii,kk}^{\alpha\alpha,\gamma\gamma}$, one can either use the Ohno–Klopman form [8, 9], or just simply the following formula:

$$\mathcal{U}_{ii,kk}^{\alpha\alpha,\gamma\gamma} = [|R_i - R_k|^2 + \mathcal{U}_{\alpha\alpha,\gamma\gamma}^{-2}]^{-1/2}. \quad (20)$$

In this way, we ensure that the Coulomb integral has the proper limits for large and small distances R_{ik} ; that is, it goes to $1/R$ for large R , and tends, for $R = 0$, to its atomic value $\mathcal{U}_{\alpha\alpha\gamma\gamma}$ which is typically of the order of the inverse of the atomic radius.

The approximation in equation (19) has been used for an arbitrary basis set; it further reduces to a simpler form if the basis is orthonormal. Such is the case for the basis that we have used for carbon [2] and silicon [7], where each atom has one 2s and three 2p orbitals. One is left with $\mathcal{U}_{ss,ss}$, $\mathcal{U}_{ss,pp}$, $\mathcal{U}_{pp,pp}$, $\mathcal{U}_{pp,p'p'}$ [10], $\mathcal{U}_{sp,sp}$, and $\mathcal{U}_{pp',pp'}$ (the last two terms being exchange integrals). Similarly, for transition metal elements with nine orbitals per atom, one has to deal with more terms, the largest of which involve d orbitals, since they are more localized. To obtain accurate values of \mathcal{U} , one could perform a fit to *ab initio* results of a given structure. We chose, however, to ‘fit’ the on-site terms of \mathcal{U} to the unbiased *atomic* calculation, since the on-site integrals do not depend much on the environment of the atom, especially in a HF formulation. As will be shown later, the results are not very sensitive to the exact values of the integrals, since a small error in a small effect does not amount to much difference, as long as the values adopted are reasonable of course. Furthermore, the fitting process is very simple for an atom.

In the case of an atom, the chemical hardness matrix η and the Coulomb integral \mathcal{U} can be identified (see equation (11)), since the basis indices are identical to the eigenstate indices. It follows that exchange terms such as $\mathcal{U}_{sp,sp}$ and $\mathcal{U}_{pp',pp'}$ are identically zero for the atom; the exchange effects are really being included in \mathcal{U} itself, as can be seen from equations (8) and (9). This, fortunately, reduces the number of parameters, and, anyway, since the TB

parameters are usually derived from a fit to DF calculations where the exchange–correlation potential is local, there is no need to include exchange integrals unless one is performing a HF calculation.

Table 1. Values in eV of the on-site Hubbard terms for carbon and silicon.

Parameter	Carbon	Carbon	Carbon	Silicon
	This work	\mathcal{U} (from [11])	U (from [11])	This work
ss, ss	10.83	11.43	16.2	8.16
ss, pp	10.37	—	14.0	7.37
sp, sp	0	—	2.30	0
pp, pp	9.93	11.11	14.6	6.76
pp, p'p'	9.93	—	13.5	6.76
pp', pp'	0	—	0.54	0

We have performed atomic calculations based on the DF formalism (in the local density approximation) for carbon and silicon atoms where the occupation numbers of the 2s and 2p levels were set to values that are real numbers near 2. In this way, one could obtain the derivatives of the total energy with respect to the occupation numbers by the finite-difference method. This in turn gives the chemical hardness matrix η via equation (10). The results obtained for C and Si are displayed in table 1. One also has the option of carrying out all calculations within the HF theory, and extracting from the chemical hardness matrix the electrostatic Coulomb integrals defined in equation (4) by using equation (9). In any case, it is possible to extract the on-site Coulomb integrals from an atomic calculation without much difficulty. For magnetic systems this could be generalized within either an unrestricted HF theory or a DF formalism, where one would have to consider two Hamiltonians, one for each spin. Omitting basis indices and leaving only spin indices, the \mathcal{U} -terms would then be defined by

$$\mathcal{H}_\sigma = \mathcal{H}_\sigma^0 + \sum_{\sigma\sigma'} \mathcal{U}_{\sigma\sigma'} \delta\rho_{\sigma'} \quad (21)$$

where \mathcal{H}_σ^0 is a reference Hamiltonian matrix which does not necessarily need to depend on σ (if, for example, it is fitted from a paramagnetic calculation). The same type of interpolation as in equation (20) can then be used, and one would again end up with an atomic calculation from which the spin-dependent on-site terms may easily be extracted.

Table 1 displays the values for the on-site parameters that we found for silicon and carbon. In the third and fourth columns we give the values obtained for the screened \mathcal{U} - and electrostatic U -integrals, respectively, from reference [11].

4. Numerical results

As a test sample, we considered C₂₀ corannulene, the bowl-shaped carbon molecule, and icosahedral Si₁₂. In what follows, we compare the results of *ab initio* calculations on singly and doubly charged molecules to the prediction of the present formalism using the \mathcal{U} -integrals described in the previous section. The geometries adopted are the same for both types of calculation, and no further geometry optimization has been done, although the addition of the charge would create some force, and slightly change the ground-state structure of the molecules.

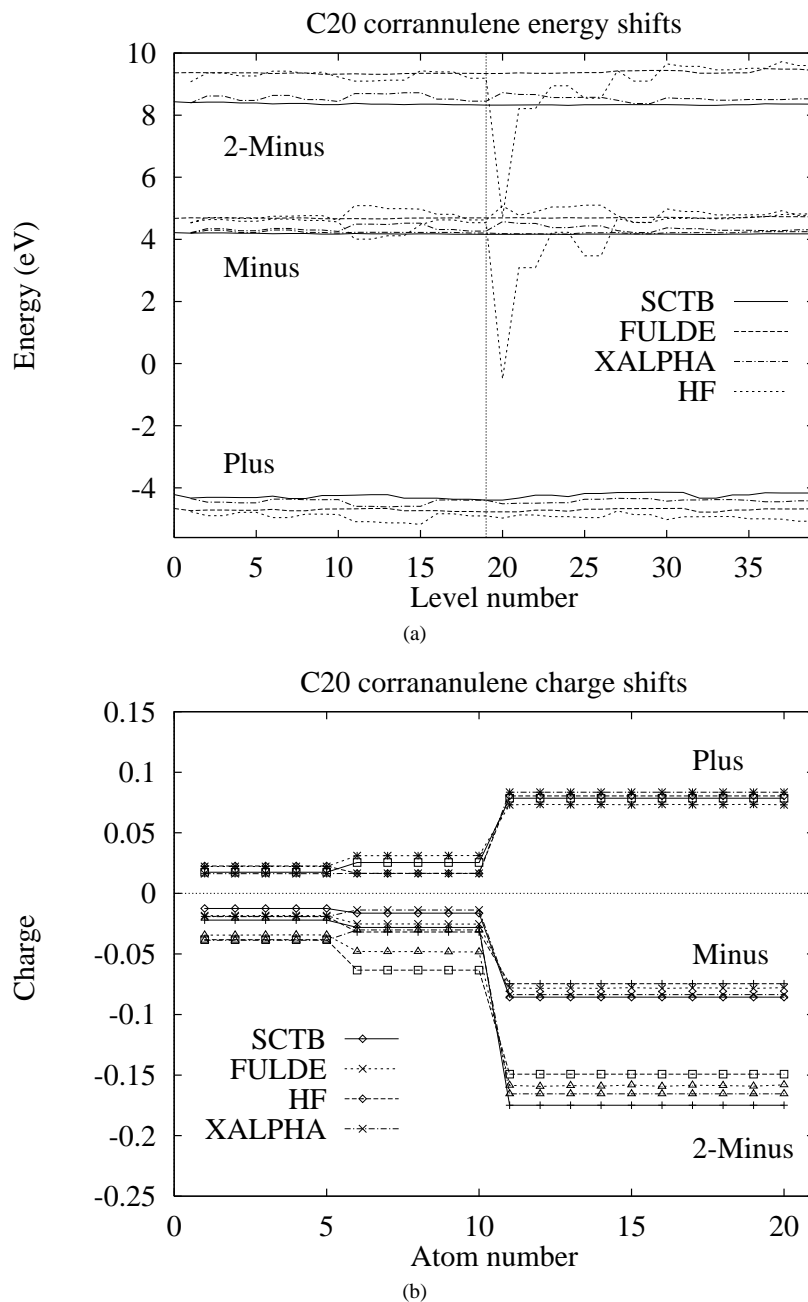


Figure 1. (a) Energy shifts of C_{20} calculated from the present self-consistent TB method compared to *ab initio* ones calculated using Gaussian 94 (HF and X_α), and another TB parameter set for U . The vertical line shows the highest occupied molecular orbital (HOMO) level. (b) Charge shifts for two TB calculations and two *ab initio* calculations (HF and X_α). In both cases, there is a good agreement between the HF results and the parameters taken from Fulde's book [11], and between the X_α results and our present parameters taken from a local density approximation (LDA) atomic calculation.

4.1. C_{20} corranulene

The often-used orthogonal parametrization of Xu *et al* [2] was adopted to treat the carbon clusters. For the singly and doubly charged molecules, rigid upward shifts of, on average, 4.17 and 8.35 eV, respectively, were found. With the same coordinates, the program Gaussian 94 [12], using the X_α exchange–correlation functional and ten basis functions per carbon atom (the 3-21G basis set), has yielded respective shifts of 4.24 and 8.54 eV on average. For comparison, Gaussian 94 was also run within the HF approximation with the same 3-21G basis set. In this case, the shifts were slightly larger, except at the Fermi level, as can be seen from figure 1. Using the electrostatic U -integrals yields a result similar to the HF method, since the HF method also uses the same type of integral. Including exchange or setting the on-site exchange integrals to zero, we find that the eigenvalues change by less than 0.1 eV, even though one exchange integral is equal to 2.3 eV. This means that the exchange terms that are of the order of 1 or 2 eV may be neglected, because the density matrix has small on-site off-diagonal terms $\delta q_{ii}^{\alpha\beta}$, and because the relevant factors for determining the shifts are mainly $U_{ss,ss}$, $U_{ss,pp}$, and $U_{pp,pp}$, which are of the same order.

One should note that the qualitative features of the eigenvalues of the neutral molecule obtained by using TB and *ab initio* methods are similar. Quantitatively, however, the three calculations yield three different spectra. Even with the same number of basis functions, different choices of the exchange–correlation potential give different results: the bandwidth of the first 40 levels around the Fermi energy for C_{20} is about 33 eV for the HF calculation, 20 eV for TB calculation, and 18 eV for the DF theory calculation. In all cases, after charging, one finds an almost rigid shift for all levels. In figure 1(b), the changes in the charge distributions for both self-consistent TB (SCTB) and HF calculations are displayed. Again, the charge distributions in the neutral case are slightly different, due to the different numbers of basis functions, and the different methods. But the error in the change in the charge distribution between those obtained using the TB method and the LDA is comparatively very small. Similarly to the eigenvalue case, we find good agreement between the shifts from our SCTB and X_α calculations on one hand, and between those from the SCTB calculations made using parameters given by Fulde [11] and the HF method on the other.

It is noteworthy that, previously, only one constant value of U was included in the treatment of charge transfer; its value was found empirically to be 4 eV for carbon systems [2] and 1 or 2 eV for silicon. But, as we have shown in table 1, the atomic calculations yield values that are almost three times these empirical values. For comparison, the shifts of the SCTB eigenvalues were also calculated with this constant value of U . We found a considerable disagreement with *ab initio* calculations for both eigenvalues and charge shifts.

4.2. The Si_{12} icosahedral molecule

As a second example, a silicon cluster, Si_{12} , with icosahedral symmetry, was also tested [13]. The TB parameters were taken from reference [7], and have the same analytic distance dependence as carbon. Again, the Coulomb integrals were taken from an identification with the chemical hardness matrix obtained from a LDA atomic calculation (see the last column of table 1). In this instance too, good agreement was found between the TB results and the DF-LDA X_α ones calculated using Gaussian 94; the shift due to the addition of a single electron was found to be 3.93 eV in the former case and 3.78 eV in the latter case. The results obtained for the energy and charge shifts are displayed in figures 2(a) and 2(b) respectively.

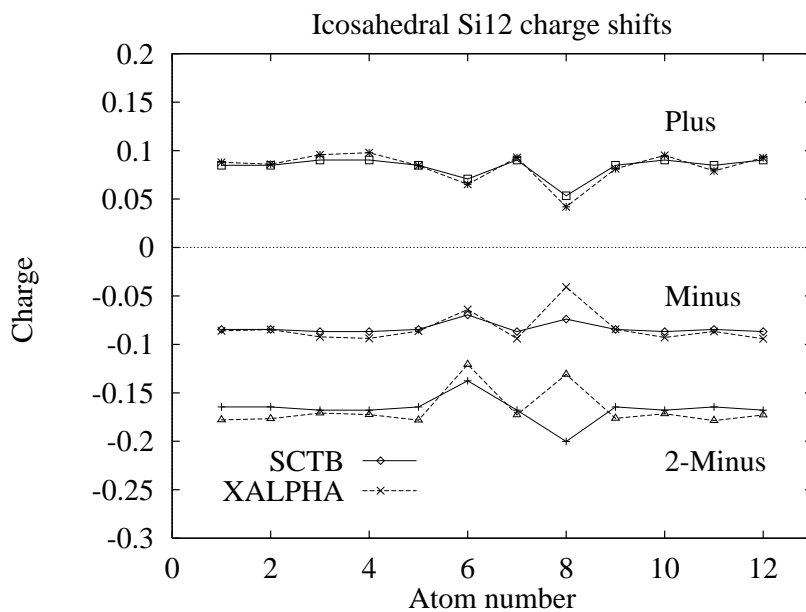
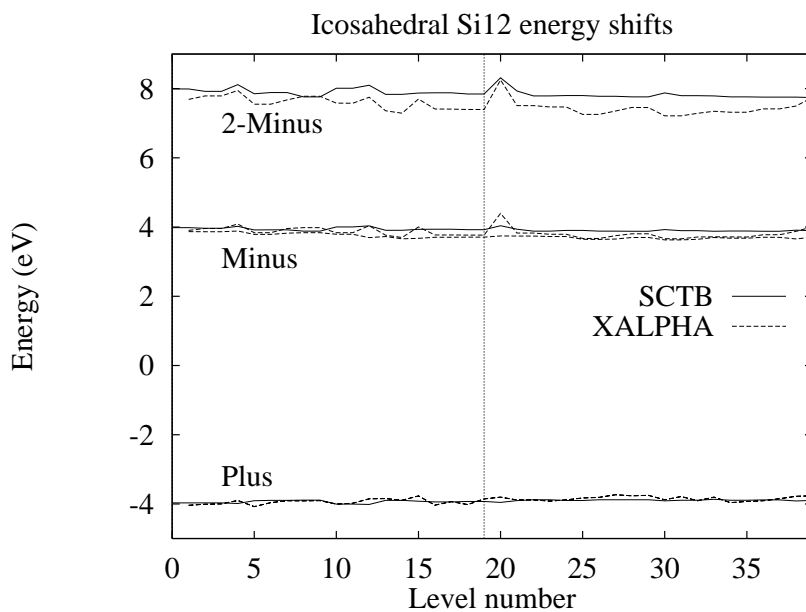


Figure 2. (a) Energy shifts of Si₁₂ calculated from the present SCTB method compared to *ab initio* ones calculated using Gaussian 94. The vertical line shows the HOMO level. (b) As (a), but for charge shifts.

5. Conclusions

The inclusion of a Hubbard term is crucial in ensuring transferability in systems with non-uniform coordination numbers. Any good parametrization should include such a term, not

only physically, but also mathematically, since the fitting of TB parameters is always carried out using bulk phase data, for which there is no charge transfer. This formulation allows one to include the effect of external fields and additional charges in a self-consistent manner. The calculations are made slightly longer because of the iterations needed to reach self-consistency. This problem can, however, be dealt with by using efficient algorithms such as that of Broyden [14], in order to reach convergence and self-consistency of the total charge after just a few iterations. It is also possible to treat magnetic systems by similar self-consistent methods (e.g. within an unrestricted Hartree–Fock formalism) once the on-site exchange parameters are known. Empirical values used in the past for \mathcal{U} were shown to be incorrect, since they cannot describe the correct charge distribution and eigenvalue shifts. A simple method was demonstrated, from which one can easily extract the on-site Coulomb terms \mathcal{U} . It was also shown that off-diagonal \mathcal{U} -terms, since they are quadratic in the overlap, can be neglected; as a consequence, only diagonal elements of the Hamiltonian matrix need to be corrected. Good agreement with *ab initio* values was found, if either the numerical value of the integral was used, as in reference [11], or they were fitted to an atomic calculation, as was done here. In both cases, despite the slight difference in eigenvalues and the charge distribution, the shifts of these quantities were very similar. The exchange parameters were irrelevant in the examples considered, but might become important for metals, for which the density matrix is long ranged.

We were also recently informed of two other self-consistent tight-binding calculations which were presented at a recent Materials Research Society meeting [15]. The treatment in the first paper, by Frauenheim *et al*, is very similar to ours, although the formalism is not based on the density matrix, and the charges are for each atom rather than each orbital. Frauenheim *et al* therefore have one \mathcal{U} -parameter for each atom, which, by the way, is not specified. Furthermore, they have neglected the off-diagonal contributions of the density matrix, which could become important for metals, in their formalism. The aim in that paper was to treat charge transfer in neutral atoms in different environments. Here, on the other hand, we show that for charged systems the eigenvalue and charge shifts are also reproduced correctly. The second paper, by Saito *et al*, treats charged fullerenes by adding a \mathcal{U} -term to the total energy. But there, again, one Hubbard parameter per C_{60} atom was used, which might be justified for their purposes. In contrast, in this work, we are interested in more detail of the electronic structure, and have considered the charge transfer for each orbital separately.

Acknowledgments

We would like to thank Professor M Sluiter and Professor K Ohno for useful discussions. KE was supported by the Virtual Laboratory of Materials Design, funded by the IBM and Hitachi corporations.

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