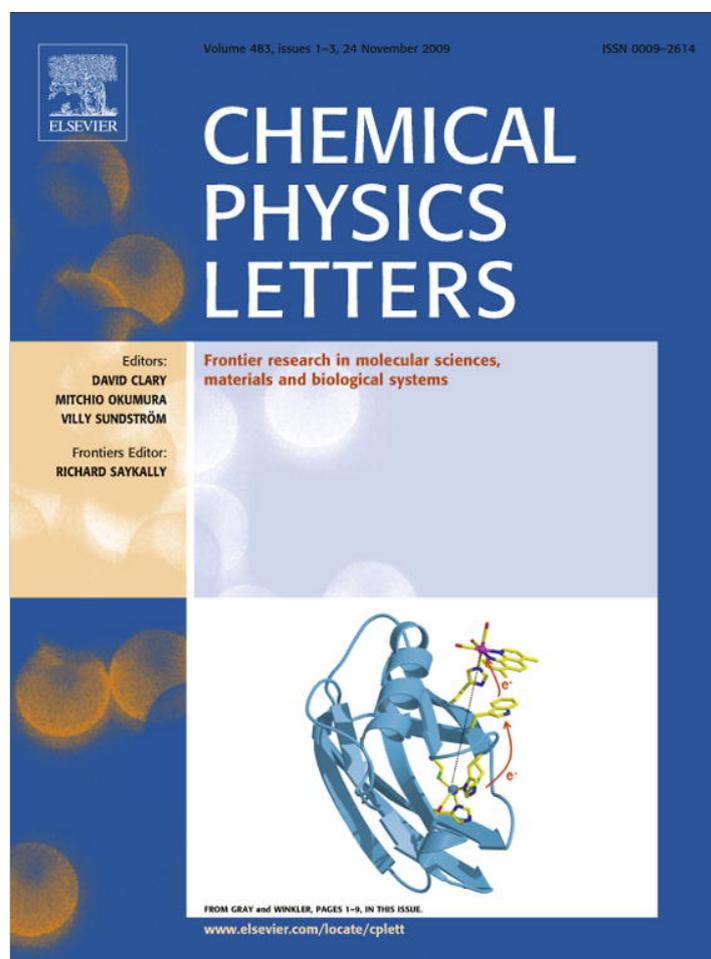


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Ring currents in azulene

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ARTICLE INFO

Article history:

Received 21 September 2009

In final form 13 October 2009

Available online 23 October 2009

ABSTRACT

We propose a self consistent polarisable ion tight binding theory for the study of push–pull processes in aromatic molecules. We find that the method quantitatively reproduces *ab initio* calculations of dipole moments and polarisability. We apply the scheme in a simulation which solves the time dependent Schrödinger equation to follow the relaxation of azulene from the second excited to the ground states. We observe rather spectacular oscillating ring currents which we explain in terms of interference between the HOMO and LUMO states.

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1. Introduction

Electronic excitations in small molecules are complex processes and from a theoretical point of view may be expected to be badly rendered in a one electron approximation. For example azulene fluoresces from the second, not the first excited state, and to describe this one must go beyond the description of the electron wavefunction in terms of a single Slater determinant [1]. On the other hand many interesting dynamical processes involve electron transport in the picosecond timescale and this is beyond the reach of modern quantum chemistry, and a challenge even for time dependent density functional theory [2]. A process of this type that we have in mind is the transfer of electrons through the π system in aromatic molecules: the so called ‘push–pull’ process. A prototypical molecule in this case is para nitroaniline (pNA) whose non-linear optical responses may be understood in terms of the push–pull process [3].

In this Letter we explore to what extent a simple, orthogonal tight binding (TB) approximation to density functional theory in the local spin density approximation (LSDA) can be usefully predictive in these matters. The model we employ is a self consistent, polarisable ion TB scheme first proposed for the study of phase transitions in transition metal oxides which are dominated by dipole and quadrupole polarisability of the anion sublattice [4,5]. We find firstly that the model quite faithfully reproduces the total polarisability of both ‘neutral’ and zwitterionic forms of pNA as well as ground and ‘excited’ states of azulene; secondly we discover a rather spectacular generation of ring currents in azulene.

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2. Model

The hamiltonian that we use is

$$\hat{H} = \sum_{\mathbf{R}L'} (\epsilon_{\mathbf{R}L}^0 \delta_{LL'} + V_{\mathbf{R}L'L'}) c_{\mathbf{R}L}^\dagger c_{\mathbf{R}'L'} + \sum_{\substack{\mathbf{R}L'L' \\ \mathbf{R} \neq \mathbf{R}'}} h_{\mathbf{R}L'L'} c_{\mathbf{R}L}^\dagger c_{\mathbf{R}'L'}, \quad (1)$$

which is expressed in a model LCAO and treated in the mean field approximation. Here, $c_{\mathbf{R}L}^\dagger$ creates an electron at an atom having position vector \mathbf{R} in orbital L with angular momentum quantum numbers $L = \{\ell m\}$. The remaining quantities appearing in (1) are defined thereby; below we show how these are obtained. Self consistency is imposed *via* charge transfers, $\delta q_{\mathbf{R}}$, at site \mathbf{R} which are defined as the difference in orbital Mulliken population between an atom at site \mathbf{R} and its neutral counterpart *in vacuo*. So if $Z_{\mathbf{R}}$ is the number of valence electrons in the free atom labelled \mathbf{R} , then

$$\delta q_{\mathbf{R}} = \sum_L \langle c_{\mathbf{R}L}^\dagger c_{\mathbf{R}L} \rangle - Z_{\mathbf{R}} \doteq Q_{\mathbf{R}0}$$

is the monopole moment of the charge transfer at site \mathbf{R} . We also permit higher multipoles to develop, in this case up to the dipole level. For $\ell > 0$, we define

$$Q_{\mathbf{R}L} = \sum_n f_n \sum_{L'L''} \bar{z}_{\mathbf{R}L}^n z_{\mathbf{R}'L''}^n \Delta_{\ell\ell''} C_{LL'L''},$$

a ‘bar’ denoting complex conjugation. Here, z are eigenvectors of the instantaneous one electron density operator $\hat{\rho}$ whose matrix elements are

$$\rho_{\mathbf{R}L'L''} = \sum_n f_n z_{\mathbf{R}L}^n \bar{z}_{\mathbf{R}'L''}^n.$$

In equilibrium or in time independent solutions of the Schrödinger equation such as we treat in Section 3, z are simultaneously the eigenvectors of the hamiltonian since in that case $\hat{\rho}$ and \hat{H} commute. In time dependent problems as in Section 4, both \hat{H} and $\hat{\rho}$

depend on time. f_n are occupation numbers, $C_{LL'}$ are Gaunt integrals and $\Delta_{\ell\ell'}$ are polarisation ‘strength’ parameters of the TB model [6]. The Madelung potential seen by an electron at site \mathbf{R} is expanded into spherical waves with coefficients

$$V_{\mathbf{R}\mathbf{L}}^M = e^2 \sum_{\mathbf{R}' \neq \mathbf{R}} \sum_{L'} B_{\mathbf{R}\mathbf{L}\mathbf{R}'L'} Q_{\mathbf{R}'L'},$$

where B is a generalised Madelung matrix [7]. Charge transfer is resisted by on-site Coulomb repulsion through the Hubbard potential,

$$V_{\mathbf{R}}^U = U_{\mathbf{R}} Q_{\mathbf{R}0}.$$

The on-site matrix elements of the hamiltonian (1) are adjusted self consistently in response to the competition between Madelung and Hubbard potentials, so that the atomic energy levels $\epsilon_{\mathbf{R}\mathbf{L}}^0$ are incremented in (1) with

$$V_{\mathbf{R}\mathbf{L}\mathbf{L}'} = V_{\mathbf{R}}^U \delta_{\mathbf{L}\mathbf{L}'} + \sum_{L''} V_{\mathbf{R}\mathbf{L}''}^M \Delta_{\ell\ell''} C_{\mathbf{L}\mathbf{L}''L''}. \quad (2)$$

At the level of monopole moments, the Madelung matrix is just $1/|\mathbf{R} - \mathbf{R}'|$ and only diagonal ($L' = L$) terms survive in (2) as simple shifts in the on-site energies. This is then equivalent to the well known SCC-DFTB method [8].

In the empirical TB approximation, we do not compute the atomic-like orbitals, instead the matrix elements of the hamiltonian are themselves parameterised. The parameters we need are the hopping, or transfer integrals $h_{\mathbf{R}\mathbf{L}\mathbf{R}'L'}$ between s and p electrons on the atoms C, O, N and H, their on-site energy levels $\epsilon_{\mathbf{R}\mathbf{L}}^0$ and the Hubbard U parameters. Hopping integrals have been taken directly from previous work on hydrocarbons by Horsfield et al. [9]. In the case of pNA where we also require C–N, C–O and N–O hopping integrals, we have used the C–C values (although the C–N factors V_x [9] are scaled by a factor of 1.1). For N–H and O–H we have again simply used the C–H values. We have adjusted the on-site energy levels and the Hubbard U parameters to reproduce the ground or ‘excited’ state dipole moments in azulene and pNA respectively. The parameters of our model which differ from those of Horsfield et al. are shown in Table 1.

3. Polarisability

Apart from drawing upon a previous TB model for hydrocarbons [9], the only ‘fitting’ so far has been to adjust the on-site terms (Table 1) so as to reproduce the static dipole moments as calculated in the LSDA. In the case of pNA rather than use the ground state dipole moment we used the dipole moment in a crudely constructed ‘excited state’. This is made by taking an electron from the HOMO and placing it in the LUMO, thus generating an electron-hole pair. The charge density is then made self consistent under this constraint. (In both ground and ‘excited states’ atomic positions are those predicted by the ground state LSDA.) This state

we will refer to as X_1 , a one electron analogue of the S_1 excited state in configuration interaction [1]. (In Section 4 we will also construct a state X_2 , by transferring an electron from the HOMO into LUMO + 1. This is the analogue of S_2 which is the initial state of the well known Kasha’s rule anomaly in azulene in which S_1 to S_0 fluorescence is suppressed [10].) The motivation behind doing this is that while this is not a proper excited state for a number of reasons, it is a well defined construction that can be made equivalently in both LSDA and in our TB model, and the outcomes compared. This provides scope to demonstrate the *predictive power* of the method. The comparison with LSDA is natural in view of the origins of the self consistent TB approximation in density functional theory. To test the model further one can apply an electric field along the molecule (again both in LSDA and TB) and observe how the dipole moment varies. Extracting the linear term provides access to the polarisability. Our results are shown in Table 2.

It is of interest to note that the ground state dipole moment in azulene points from the five to the seven membered ring, while its sign is reversed in X_1 (see Fig. 1). This is easily explicable within simple Hückel theory [13] and it is therefore no surprise that this fact is properly rendered in the TB approximation. What is remarkable however is how well the TB model follows the LSDA in the quantitative reproduction of the polarisability.

4. Ring currents in azulene

Armed with this model we are motivated to study electron transfer. As an initial demonstration we have followed the transfer of electrons across the azulene π system as the X_2 excited state is made to decay into the ground state. We approach this simulation using time dependent TB theory [14]. In this instance we start the molecule in X_2 by putting an electron from the HOMO into LUMO + 1 and making the density operator self consistent under this constraint. We used a slightly modified geometry compared to that in Section 3 by relaxing the atoms in our tight binding model with a model repulsive pair potential, so in the present section our molecule has dipole moments of -0.418 D and -0.466 D in X_1 and X_2 , respectively. Since we have no dissipation in our simple model, we take the ground state density operator to be $\hat{\rho}_0$ and we develop the following dynamics by solving the time dependent Schrödinger equation in terms of the instantaneous density operator $\hat{\rho}$,

$$\frac{d}{dt} \hat{\rho} = (i\hbar)^{-1} [\hat{H}, \hat{\rho}] - \Gamma(\hat{\rho} - \hat{\rho}_0).$$

Square brackets indicate a commutator, and Γ is a damping parameter, which in the present simulation we take to be $\Gamma^{-1} = 500$ fs. We set Γ to zero when multiplying *diagonal* matrix elements of $(\hat{\rho} - \hat{\rho}_0)$; this is necessary to preserve the continuity equation. In

Table 1

Parameters of our tight binding model for p-nitroaniline. Atomic Rydberg units are used throughout. Values in parentheses are those for azulene, note that we use the monopole charge model for azulene ($A_{spp} = 0$) whereas the polarisability is found to be essential to describe the dipole moment in pNA correctly.

| | C | N | O | H |
|----------------|------------------|-------|-------|------------------|
| ϵ_s^0 | -1.43 (-1.42) | -0.99 | -1.45 | -1.00 (-1.00) |
| ϵ_p^0 | -0.92 (-0.81) | -0.55 | -1.04 | - |
| U | 1.3 (1.2) | 1.2 | 0.77 | 1.0 (1.2) |
| A_{spp} | -0.5 (0) | -1.0 | -0.84 | - |

Table 2

Calculated dipole moments (in Debye) and polarisabilities of azulene and pNA using our TB model. GS and X_1 refer to ground and ‘excited states’, respectively. Values in parentheses are calculations using LSDA and those in brackets are experimental values as quoted by Hinchliffe and Soscún [1]. The agreement with experiment is probably fortuitous [1]; what is more significant in this context is the comparison between TB and LSDA.

| | Azulene | | pNA | |
|-----------------------------|--------------------------|-------------------|----------------|---------------|
| | GS | X_1 | GS | X_1 |
| p (D) | 0.75 (0.69) [0.80] | -0.375 (-0.53) | 4.38 (4.1) | 6.63 (6.4) |
| α (\AA^3) | 12.6 (14.1) [15.7] | 12.4 (14.0) | 14.5 (13.1) | 23 (25) |

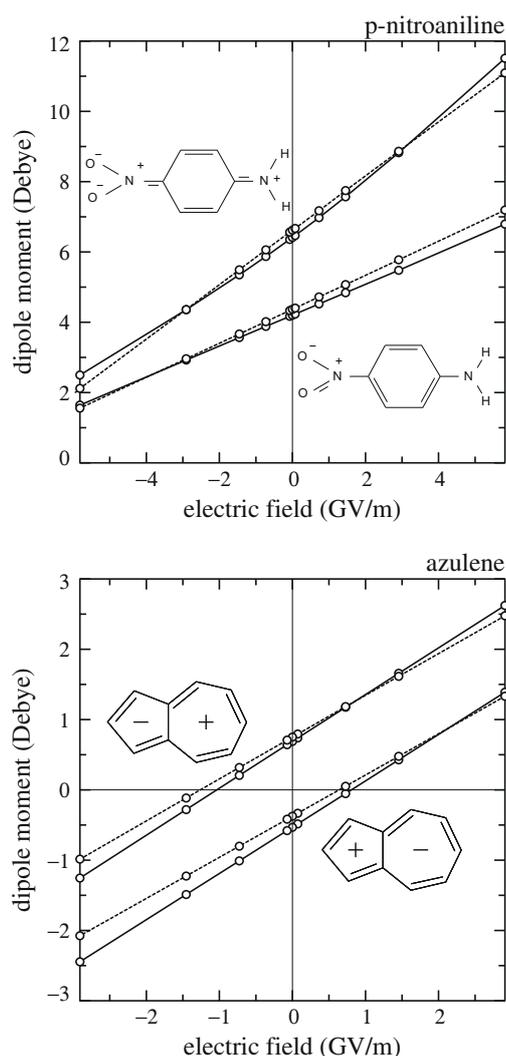


Fig. 1. Dipole moment as a function of applied electric field calculated using LSDA, solid lines, and TB, dotted lines. The lower figure shows azulene and the upper set of lines refer to the ground state and lower set to the excited state. The upper figure shows pNA; the lower set are the ground state and the upper set the 'zwitterionic' first excited state. Note the essentially linear nature of these curves: the slopes furnish us with the molecular polarisability (see Table 2). LSDA calculations are made using a molecule Lmro program [11,12]. In this figure and in Table 2 the geometry of the molecule is that obtained by a static relaxation in the LSDA.

this way the density matrix acquires complex matrix elements, the imaginary parts of which are responsible for the *bond current* flowing, say, from atom **R** to atom **R'** [15]

$$j_{RR'} = \frac{2e}{\hbar} \text{Im} \sum_{LL'} H_{R'L'RL} \rho_{RLR'L'}$$

$H_{R'L'RL}$ being a matrix element of \hat{H} in the LCAO. Fig. 2 shows some results of the simulation. If we concentrate first on the upper left panel, we see that the lower curve, which follows the excess number of electrons on the rightmost atom, indicates the flow of negative charge from right to left as the excited state whose dipole moment points from right to left decays into the ground state whose moment is reversed (see Fig. 1). At first sight this curve is as expected and rather featureless except careful study shows some apparent ripples or anomalies once the decay is practically achieved after about a picosecond. These ripples appear greatly amplified if one examines the excess charge on one of the atoms which are shared by both five- and seven-membered rings. This is seen in

the upper curve of the top left hand panel, showing quite amplified and regular structure. If we zoom in on the time scale in the top right hand panel we find that both curves are showing very regular oscillations at roughly femtosecond frequencies. In particular the upper curve shows that charge is transferring back and forth across the bond that connects the two rings. The lower two panels reinforce this interpretation by showing the π -bond current flowing through the bridging bond. Quite evidently this is oscillating and the clear inference, confirmed by detailed study of the charges and currents, is that ring currents are developed in the azulene molecule having counter directions in each ring. Furthermore the directions of current are changing with a period of about 2.5 fs. We find this frequency to be consistent throughout the time of the simulation. It is notable firstly that this appears to happen in bursts separated by relative quietude on a timescale of some hundreds of femtoseconds, which may well reflect the beating of two closely separated frequencies; and secondly that the oscillations do not get going until many hundreds of femtoseconds have elapsed after the start of the simulation. This delay in the onset of the phenomenon would have made it difficult to predict using first principles simulation methods. It is notable also that we are not able to induce these currents in a similar manner in naphthalene. This phenomenon is not an artefact of the damped dynamics. The observed frequencies are largely independent of Γ ; moreover if we set Γ smoothly to zero once the oscillations are established in a simulation, then these continue endlessly at the same frequencies.

We are uncertain whether these ring currents could be observed experimentally since although the current is very large (tens of microamps) in view of the small molecular area the associated magnetic fields will be extremely small. In reference to Fig. 1 it is suggestive that rather than preparing the molecule in an excited state one could obtain the effect after applying a static electric field to reverse the dipole moment. Indeed one may cause these currents to resonate in a suitably oscillating external electric field [16]. Ring currents have been proposed as the effect of a *static* magnetic field by Steiner and Fowler [17] and even counter rotating currents have been found [18]—in this case one ring current counter rotating within a larger ring current.

5. Discussion

It is gratifying that the simple TB model is able to give a quantitative rendering of the polarisability of small molecules compared to LSDA calculations. Our model extends the scheme proposed by Horsfield et al. for the study of hydrocarbons in that we go beyond the approximation of local charge neutrality. In addition our model goes beyond the SCC-DFTB method [8] by the inclusion of atomic polarisation (in this work to the dipole level). We believe that this is an essential ingredient in the description of pNA, while azulene (and presumably other hydrocarbons) is quite well modelled at the monopole level. We therefore propose our scheme as a useful means of studying electron transport at the picosecond timescale.

The frequency of the oscillating ring currents matches closely the HOMO–LUMO gap in azulene, suggesting that the origin of these currents is HOMO–LUMO interference. Indeed, explicit calculations show that time evolving linear combinations

$$|\psi(t)\rangle = a e^{-iE_0 t/\hbar} |0\rangle + b e^{-iE_1 t/\hbar} |1\rangle$$

with constant $ab \neq 0$, carry oscillating ring currents with an opposite sense in different rings, exactly as seen in our simulations. Here, E_0 and E_1 are the one electron energies of the HOMO and LUMO molecular orbitals respectively while $|0\rangle$ and $|1\rangle$ are the associated eigenvectors; for definiteness we have taken the orbitals from the self consistent ground state of the molecule. Alternatively since the HOMO and the LUMO (and indeed LUMO + 1) reside entirely

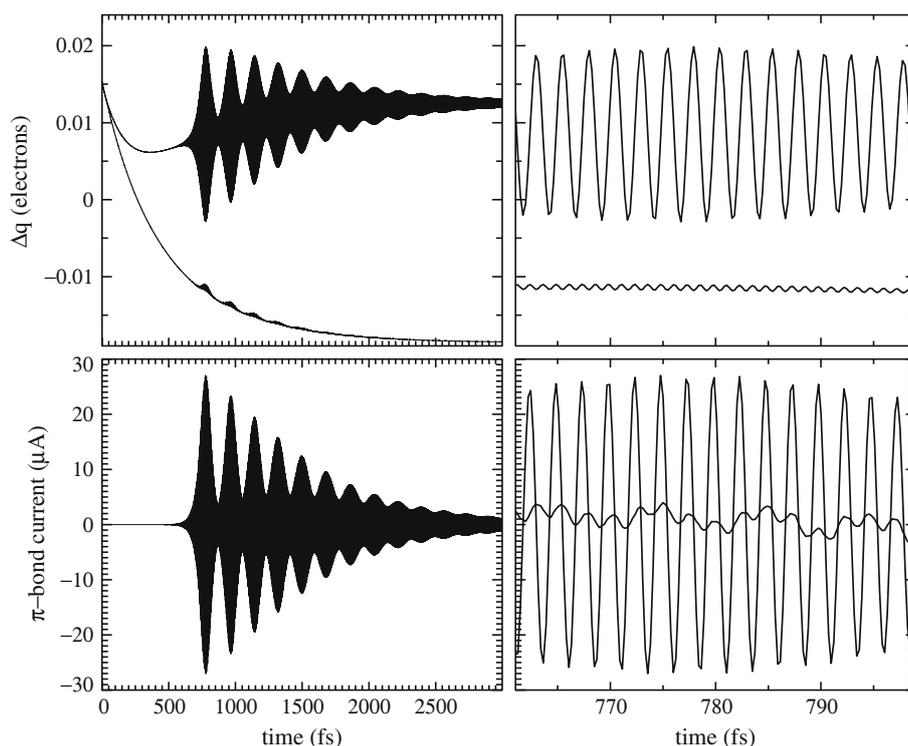


Fig. 2. Charge transfer and bond current as a function of time in the relaxation of the X_2 excited state in azulene. The upper panels show the excess number of electrons on a 'bridge' atom and on the rightmost atom in the seven-membered ring (lower curve). The lower panels show the π -bond current in the 'bridge' bond. In the lower right panel, the smaller amplitude oscillations are those from an identical simulation having X_1 as initial state; the current has been multiplied by 1000.

within the π subsystem, the problem can also readily be solved analytically within first order perturbation theory, with the bridge bond treated as the perturbation; however we do not pursue this idea further here. To gain insight into the mechanism behind the actual generation of the currents we make the following observations. (i) The currents do not appear for non-interacting electrons. (ii) They also do not appear if the geometry has perfect reflection symmetry across the longitudinal axis of the molecule. (In the simulations a small amount of asymmetry arises naturally, due to limitations of the initial structural relaxation.) (iii) Finally, and at first sight paradoxically, the ring currents are absent, or at least 1000 times smaller, if we start directly from X_1 (see Fig. 2).

These observations can be rationalised as follows. To lowest multipole order the dipole moment of the molecule sets up a homogeneous internal electric field along the longitudinal z axis. As the transition to the ground state proceeds, this field changes direction. Thus, during the process the molecule is effectively subjected to a slowly varying perturbation $\alpha(t)z$ with $\alpha(0) = 0$. Examination of the HOMO, LUMO and LUMO + 1 eigenvectors, $|0\rangle$, $|1\rangle$ and $|2\rangle$, reveals that the only non-vanishing matrix element of the dipole operator in the basis of these three states is $\langle 0|z|2\rangle$.

Therefore if we start from X_2 then at some point during the decay to the ground state, α which is by now non-zero will produce coherent mixtures of $|2\rangle$ and $|0\rangle$ causing accompanying charge and bond current oscillations to attempt to develop. But these mixtures carry bond currents of a different type which we might call 'longitudinal', with bond currents in corresponding bonds across the z -axis having the same sign along z and thus opposite sign along the angular coordinate in the ring, leading to local charge accumulation. The electron–electron repulsion, embodied in U , resists this charge accumulation. Instead, U tries to enforce continuity of current, by attempting to turn any longitudinal current into a ring current. A small symmetry breaking at this point helps the U achieve its goal and ring currents develop. In this light, the ring currents may be viewed as an attempt by the system to minimise

the local charge build-up that would otherwise develop due to internal fluctuations. This does not happen starting from X_1 , because the primary step above is missing, namely $\langle 0|z|1\rangle = 0$. In summary, the ring currents are associated with interference between the HOMO and LUMO, $|0\rangle$ and $|1\rangle$, and hence their frequency is set by the HOMO–LUMO gap; conversely in the first instance their initiation is due to interference between $|0\rangle$ and $|2\rangle$ whose associated bond currents run along the axis of the molecule. It is the electron–electron interaction which drives longitudinal currents into the observed ring currents.

The beats, we believe, are due to a small effective 'smearing' of E_0 and E_1 , as a result of on-site energy oscillations caused by the interaction potential (2). Evidence for this is that the beat frequency saturates with increasing U . Finally, the ring currents do not develop in naphthalene because in that case the HOMO and LUMO have vanishing amplitudes at the bridge sites. An interesting question is whether molecular vibrations destroy or enforce the ring currents. From some preliminary observations, we believe that the ring currents survive, but this question is left for further investigation in the future.

6. Conclusions

We have proposed a self consistent, polarisable ion model as a tool in molecular simulations. Perhaps surprisingly our simple model with a minimum of fitting is able to predict accurately the polarisability of the two molecules we have described here. We have gone on to demonstrate its application in time dependent simulations which have revealed a remarkable phenomenon of oscillating ring currents in azulene. While static ring currents are well known to arise under a constant magnetic field [17,18] as in NMR, we believe this may be the first prediction that counter rotating, oscillating ring currents may be generated not only by laser fields [16] but also during the relaxation of excited states.

Acknowledgements

This work was supported by EPSRC under grants GR/S80165, EP/C006739 and EP/G012156. ATP wishes to thank the Royal Society for support, and also Prof. A. Oesmann.

Appendix A. Supplementary material

Supplementary data associated with this Letter can be found, in the online version, at [doi:10.1016/j.cplett.2009.10.041](https://doi.org/10.1016/j.cplett.2009.10.041).

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