On the electronic structure of benzene and borazine: an algebraic description

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Abstract
The spectrum of a hexagonal ring is analysed using concepts of group theory and a tight-binding model with first, second and third neighbours. The two doublets in the spectrum are explained with the $C_3$ symmetry group together with time-reversal symmetry. Degeneracy lifts are induced by means of various mechanisms. Conjugation symmetry breaking is introduced via magnetic fields, while $C_3$ breaking is studied with the introduction of defects, similar to the inclusion of fluorine atoms. Concrete applications to benzene and borazine are shown as an illustration of our description. Wave functions are described in connection with partial or full aromaticity.

Keywords: borazine, benzene, symmetry bases, algebraic methods

1. Introduction
The electronic structure of benzene, understood in terms of valence orbitals, has been known to chemists for a long time [1] and even exposed in anecdotal fashion in [2]. Quite recently, an increased amount of research on this subject involving the more elusive borazine [3]—also known as the inorganic benzene—shows a pursuit for the best description regarding its electronic structure. For example [4], the vibrational levels of borazine were obtained experimentally with neutron scattering techniques, together with density functional theory (DFT) calculations in bulk. The aromatic structure of these rings has been discussed for some time [5] with increasingly detailed techniques [1]. While delocalisation in benzene is now incontrovertible—when degeneracy is correctly considered—the case of borazine seems to be more consistent with partial localisation or moderate aromaticity. DFT was also employed for borazine [6], supporting this view. It should be mentioned that long-standing experiments regarding the atomic and electronic configurations of these molecules have provided a solid basis for theoretical discussions: the lower part of the electronic spectrum in benzene was studied previously in [7] with photoelectron spectroscopy, and electron impact experiments were reported in [8]. Older calculations by Moskowitz [9] suggested the use of symmetry-adapted bases as well as $\pi - \sigma$ interactions between orbitals, in order to understand the resulting electronic clouds. As a conclusion, even when the corresponding models are improved in detail, the groups $C_6$ and $C_3$ of these molecules and their adapted functions should never be disregarded.

Our goal in this work is to provide a simple algebraic description of energy levels and wave functions that reasonably reproduce the known properties of 6-rings. We shall work with group theoretical concepts that include the representations of cyclic groups $C_1$, $C_6$, $Z_2$ and the introduction of antibunitary operators in connection with magnetic perturbations. Also, a supersymmetry $N = 2$ related to a $Z_2$-grading [10, 11] will make its appearance in a six-dimensional Hilbert space. Our treatment will be closely connected to specific matrix realisations and we shall keep calculations as explicit as possible, for the sake of clarity. We should also mention
that, despite the extensive use of Galois fields in highly symmetric situations, their correct composition in phase space was only given recently in [12–16] for odd cases and [17] for even cases, which are of particular importance for 6-rings, as the group decomposition \( C_6 = C_3 \times Z_2 \) trivially shows.

As a further motivation of our work, the simplicity of the present approach suggests the use of simple molecular orbitals for other computational applications. Our recent incursion into hexagonal structures [17, 18] sprouted some interest on exotic effects emerging even in the simplest of descriptions: tight-binding models of a single electron. In the realm of quantum emulations, realisations in microwaves [19–23], and elastic waves [24–26] have shown the universality of frequency spectra produced by highly symmetric structures, such as hexagon and triangle symmetries, together with their moderate breaking.

The structure of the paper is as follows. Section 2 presents the tight-binding ring model benzene-like molecules. The energy levels are obtained analytically and the presence of two doublets are identified with time-reversal symmetry. A discrete version of the continuity equation is studied and expressions for electronic currents revolving around the molecule are obtained. Numerical calculations for benzene are developed using the parameters reported in the literature. The borazine model is studied in section 3. The Hamiltonian is presented as a partitioned 2 \( \times \) 2 diagonal matrix where each block is solvable by radicals. Numerical calculations for borazine are presented. Finally, in section 4, a dynamical supersymmetry (SUSY) in the ring is found and presented. The dynamical SUSY provides a theoretical explanation of the spectral symmetry under level reflection around an isolated carbon atom energy. This holds for both benzene and borazine spectra, even in a globally broken \( C_3 \) configurational symmetry. Conclusions are given in section 5.

2. Benzene and the \( C_6 \) group

The molecular structure of benzene was a subject of study since the second half of the XIX century, when the chemist August Kekulé recognised that there should exist a symmetry inherent to the molecule and elucidated the hexagonal geometry of benzene. With the development of the quantum theory, the atomic structure of benzene became clearer [27, 28]. Each of the six carbons in the molecule possesses three \( sp^2 \) hybrid orbitals, which are coordinated with other two \( C \) atoms and with the \( s \) orbital of the H atom, leading to \( \sigma \) states. The six \( p \), atomic orbitals of the C atoms perpendicular to the molecular plane, form \( \pi \) bonds; the six electrons corresponding to these orbitals are delocalised when found in stationary states as they do not belong to any particular \( C \) centre. The borazine model can be constructed in a similar way to benzene, where the orbital hybridisation \( sp^2 \) is proposed to explain the molecular structure, despite the fact that internal angles differ from those of a perfect hexagonal geometry [29]. We emphasise that the role of symmetry and algebraic methods should never be underestimated, as their neglect might lead to unusual predictions regarding the localisation of electrons around atomic centres [1] even after a diagonalization takes place.

In this section a tight-binding model is presented using a hexagonal ring with localised wave functions around each site. It is reasonable to assume that atomic orbitals can be employed as examples of highly localised states as starting points for a suitable basis, i.e. the Hückel approach. Here it should be mentioned that some analogues of Wannier functions have been known in chemistry for a long time [30–32]. However, it is difficult to find an analogue of a discrete Wannier transform for \textit{periodic boundary conditions} applied to molecules with polygonal symmetry, where the periodicity is realised by the molecular ring. Specifically, in this work we shall find that the resulting wave functions associated with polygonal symmetry groups naturally provide such a generalisation.

On quantitative grounds, we justify our approximations by employing on-site energies of C atoms of \(-8.97 \) eV [33], nearest couplings of \( 2.7 \) eV for C–C at a distance of \( 1.4 \) Å [34] consistent with the band structure of graphene and its Fermi velocity [35], nearest couplings of \( 1.95 \) eV between N–B that are consistent with the electronic bands of boron nitride, and exponential decay of hopping integrals with the distance between atomic centres. It should be noted that experimental values of the energy distance between a singlet and a doublet in benzene (both \( \pi \) orbitals) were reported [36] as \((12.1 – 9.3) \) eV = 2.8 eV, which are also consistent with our results, as long as the on-site energy is also corrected by adding between \( 5 \) eV and \( 6 \) eV accounting for Coulomb repulsion of electron charges at a distance of \( 1.4 \) Å. Our ‘back of the envelope’ estimate for a hollow charged sphere yields \((1/2) \times 10 \) eV, while a solid ball of the same radius has an energy of \((3/5) \times 10 \) eV. For a ring, we expect a similar geometric factor. With our simplified set of parameters, we may also introduce a defect, simulating the presence of a fluorine atom, as considered by [7] and [37].

Although the discussion above takes care of Coulomb repulsion between orbitals of the same kind, other questions can be raised regarding the interaction between \( \pi \) and \( \sigma \) orbitals. While it is recognised that the presence of the \( \sigma \) bonds has a repelling effect on the external \( \pi \) orbitals, we argue that this is a second order effect coming from a small perturbation. Indeed, by (anti)symmetry considerations, the corresponding matrix elements of a fully interacting Hamiltonian of at least two bodies can be estimated in magnitude according to the inequality below:

\[
\int dV_1 dV_2 \, \pi_n(r_1) \sigma_n(r_2) e^{i \pi_n H_{\pi_n}(r_1)} \sigma_n(r_2) \pi_n(r_1) \ll \int dV_1 dV_2 \, \pi_n(r_1) \sigma_n(r_2) H_{\pi_n}(r_1) \sigma_n(r_2),
\]

which is the result of the antisymmetry of the products \( \pi_n(r_1) \sigma_n(r_2) \) and \( \sigma_n(r_2) \pi_n(r_1) \) with respect to the molecular plane. With these considerations, we shall focus on the external levels only.
2.1. Multiple neighbour tight-binding model

The first system of study is a 6-ring where all the sites are equal; this corresponds to the benzene case, see figure 1. We start with a multiple-neighbour model – see figure 2 panel b) – and write the Hamiltonian $H$ in matrix representation as:

$$
H_{ij} = \begin{pmatrix}
\epsilon & \Delta_{12} & \Delta_{13} & \Delta_{14} & \Delta_{15} & \Delta_{16} \\
\Delta_{12}^* & \epsilon & \Delta_{23} & \Delta_{24} & \Delta_{25} & \Delta_{26} \\
\Delta_{13}^* & \Delta_{23}^* & \epsilon & \Delta_{34} & \Delta_{35} & \Delta_{36} \\
\Delta_{14}^* & \Delta_{24}^* & \Delta_{34}^* & \epsilon & \Delta_{45} & \Delta_{46} \\
\Delta_{15}^* & \Delta_{25}^* & \Delta_{35}^* & \Delta_{45}^* & \epsilon & \Delta_{56} \\
\Delta_{16}^* & \Delta_{26}^* & \Delta_{36}^* & \Delta_{46}^* & \Delta_{56}^* & \epsilon
\end{pmatrix},
$$

where $\Delta_{ij} = \Delta_{ji}^*$ in Hermitian models (electrons are neither gained nor lost from the system, so probability is conserved). The Schrödinger equation possesses time-reversal symmetry if all couplings $\Delta_{ij}$ are real. Since overlaps are given by

$$
\Delta_{ij} = \int \Psi_i^*(x)H\Psi_j(x)dx,
$$

this means that a Hamiltonian $H = (p^2/2m) + V(x)$ for a single electron without magnetic fields contains $\Delta_{ij} \in \mathbb{R}$ if and only if $\Psi \in \mathbb{R}$. This is indeed the case if the function $\Psi_i(x) = \langle \Phi_i^I | \langle \Phi_i |$ localised around site $i$, corresponds to a bound state of an isolated carbon atom, or in general, a state without outgoing probability current.\(^4\)

Since our first approach to the problem corresponds to a highly symmetric configuration (such as a regular hexagon) we start by constraining the couplings $\Delta_{ij}$. A translation operator modulo 6 consists of a rotation around the hexagon centre by $\pi/3$ radians. This operation is represented by $\hat{T}|i\rangle = |(i + 1) \mod 6\rangle$, $\hat{T}^3 = \hat{T}\hat{T} = 1$, $[\hat{T}, \hat{T}^\dagger] = 0$ and

\(^4\) Once more, we may resort to references [31, 32] for more rigour.
with \(|i\rangle\) the canonical basis, we have

\[
\hat{T} \equiv \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.
\]

(4)

For \(\hat{T}\) to be a symmetry of \(H\), one must have \([H, \hat{T}^n] = 0\) for all \(q = 1, \ldots, 6\). The Abelian group \(C_6\) then arises from \(\{1, \hat{T}, \hat{T}^2, \hat{T}^3, \hat{T}^4, \hat{T}^5\}\). Also, the space inversion 1 \(\leftrightarrow\) 2, \(2 \leftrightarrow 6,\) \(3 \leftrightarrow 5,\) \(4 \leftrightarrow 4,\) \(5 \leftrightarrow 3,\) \(6 \leftrightarrow 2\) is a symmetry of \(H\), but it does not commute with \(\hat{T}\). So now all secondary diagonals in \(T\) must have equal elements, leading to the notation

\[
H \equiv \begin{pmatrix}
\epsilon & \Delta_1 & \Delta_2 & \Delta_3 & \Delta_4 & \Delta_1 \\
\Delta_1 & \epsilon & \Delta_2 & \Delta_3 & \Delta_4 & \Delta_1 \\
\Delta_2 & \Delta_1 & \epsilon & \Delta_3 & \Delta_4 & \Delta_1 \\
\Delta_3 & \Delta_2 & \Delta_1 & \epsilon & \Delta_4 & \Delta_1 \\
\Delta_4 & \Delta_3 & \Delta_2 & \Delta_1 & \epsilon & \Delta_1 \\
\Delta_1 & \Delta_4 & \Delta_3 & \Delta_2 & \Delta_1 & \epsilon
\end{pmatrix},
\]

(5)

where the subscript in \(\Delta\) now denotes the neighbouring sites; obviously there is no \(\Delta_6\). In this notation

\[
H = \epsilon + 3 \sum_{n=1}^{3} (\Delta_n \hat{T}^n + \Delta_n (\hat{T}^\dagger)^n),
\]

(6)
as the reader may readily verify by using the explicit powers of \(\hat{T}\). The following matrix relations will be useful

\[
\hat{T}^4 = \begin{pmatrix}
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0
\end{pmatrix} = (\hat{T}^\dagger)^4,
\]

(7)

Since \(C_j^q = \exp(-i\pi q/3)C_{(j-1)\mod 6}^q\) and the normalisation is \(1/\sqrt{6}\), the coefficient reads

\[
C_j^q = e^{-i\pi q/3}/\sqrt{6} \quad i = 1, \ldots, 6.
\]

(9)

The explicit coefficients \(9\) together with \(|q\rangle\) above already constitute the eigenfunctions of the problem. Now we apply \(H\) to our expression for \(|q\rangle\) and find easily that

\[
H|q\rangle = \left\{ \epsilon + 3 \sum_{n=1}^{3} (\Delta_n e^{i\pi q/3} + \Delta_n e^{-i\pi q/3}) \right\}|q\rangle,
\]

(10)

thus the energy becomes

\[
E_q = \epsilon + 3 \sum_{n=1}^{3} \Delta_n \cos\left(\frac{\pi q n}{3}\right).
\]

(11)

This shows that for multiple neighbours with arbitrary couplings, the spectrum has certain properties inherent to the symmetry, and not to the specific details of the overlaps \(\Delta_n\) related to tunnelling. Therefore the explicit expression for tunnelling rates between sites is at this point irrelevant. For instance, we have that if \(q \leftrightarrow -q\) then \(E_q = E_{-q}\). But \(-q = (6 - q) \mod 6\) according to \(11\), therefore the following pairs are degenerate \(q = 1, 5; \quad q = 2, 4\) while \(q = 3, q = 6\) are singlets.

2.2. Magnetic field piercing molecular planes

Now we introduce a magnetic field orthogonal to the molecular plane. Going back to our single-electron Hamiltonian

\[
H = \frac{[p - (e/\hbar)A]^2}{2m} + V(x) = H^* + \frac{1}{2m} \left(\frac{e}{\hbar}\right)^2 \nabla^2
\]

(12)
due to the presence of terms \((e/2mc)p \cdot A\) and \((e/2mc)A \cdot p\) when the square is expanded (evidently \(p^* = -i\hbar \hat{\nabla}^* = -i\hbar \nabla = -p\)).

From here and with the tight binding representation of \(H\) limited to a single carbon valence orbital (our \(6 \times 6\) matrix) we find that \(\Delta_{ij}\) cannot be real any more. To see the relation with a magnetic field, we must apply a unitary transformation that removes all the phase factors of \(\Delta_{ij}\) as much as possible. If the transformation

\[
U_{\text{gauge}} = \text{diag}\{e^{i\phi_1}, \ldots, e^{i\phi_6}\}, \quad H' = U_{\text{gauge}} H U_{\text{gauge}}^{-1}
\]

(13)
removes all phases, then there cannot be a magnetic flux through the molecule, and no overall effect can be found in the spectrum. (In passing, we note that for open chains this is always the case, so the presence of closed loops in the coupling diagram is essential). In contrast, if a phase-factor always remains after \(U_{\text{gauge}}\) is applied, then we may have at least a certain element \(\Delta_{ij} e^{i\phi_j}\) where \(\phi_j\) has accumulated all phases in \(H\), to give

\[
H' = \begin{pmatrix}
\epsilon & \Delta_1 & \Delta_2 & \Delta_3 & \Delta_2 e^{i\phi_2} & \Delta_3 e^{i\phi_2} \\
\Delta_1 & \epsilon & \Delta_2 & \Delta_3 & \Delta_2 & \Delta_3 \epsilon \\
\Delta_2 & \Delta_1 & \epsilon & \Delta_2 & \Delta_3 e^{i\phi_2} & \Delta_3 e^{i\phi_2} \\
\Delta_3 & \Delta_2 & \Delta_1 & \epsilon & \Delta_2 & \Delta_3 \epsilon \\
\Delta_2 e^{-i\phi_2} & \Delta_3 & \Delta_2 & \Delta_1 & \epsilon & \Delta_2 \\
\Delta_3 e^{-i\phi_2} & \Delta_2 & \Delta_3 e^{-i\phi_2} & \Delta_2 & \Delta_1 & \epsilon
\end{pmatrix}.
\]

(14)
However, for notational simplicity, we write the Hamiltonian $H$ in a gauge such that
\[
\Delta_n = e^{i\phi_n}\lvert\Delta_n\rvert
\]
for all couplings. With this, the new Hamiltonian becomes
\[
H = \epsilon + \sum_{n=1}^{3} (e^{i\phi_n}\lvert\Delta_n\rvert \hat{T}_n + e^{-i\phi_n}\lvert\Delta_n\rvert (\hat{T}_n)^\dagger).
\]

It is remarkable that $|q|$ still solves the eigenvalue problem in this case, producing thus
\[
E_{q}(\{\phi_1\}) = \epsilon + 2\sum_{n=1}^{3}\lvert\Delta_n\rvert \cos\left(\frac{\pi q n}{3} + \phi_n\right),
\]
where $E_{q}(\{\phi_1\})$ is the flux-dependent energy. As the reader may see, the property $q \mapsto -q$ is now broken:
\[
E_{-q}(\{\phi_1\}) = \epsilon + 2\sum_{n=1}^{3}\lvert\Delta_n\rvert \cos\left(-\phi_n + \frac{\pi q n}{3}\right)
\]
\[
= \epsilon + 2\sum_{n=1}^{3}\lvert\Delta_n\rvert \cos\left(\frac{\pi q n}{3}\cos\phi_n + \sin\left(\frac{\pi q n}{3}\right)\sin\phi_n\right).
\]

The energy gap between $E_q$ and $E_{-q}$ is
\[
E_{-q} - E_q = \Delta E = 4\sum_{n=1}^{3}\lvert\Delta_n\rvert \sin\phi_n \sin\left(\frac{\pi q n}{3}\right)
\]
and now we see that $\sin(\pi q n/3) = -\sin(-\pi q n/3)$ produces a difference. We can plot the eigenphases of the $C_6$ group as shown in figure 3 to visualise schematically the level structure of the ring, where the degenerate states possess the same projection in the real axis. The conclusion is that $E_{-q}(\{\phi_1\})$ and $E_{q}(\{\phi_1\})$ are no longer degenerate and the two doublets are split by an amount controlled by the field $\phi_n$. For example, if a nearest-neighbour model is considered, i.e. $\Delta_1 \equiv \Delta$, $\Delta_2 = \Delta_3 = 0$, then a rotation of the phases expresses the level repulsion quantitatively as shown in panel (b) of figure 3.

2.3. Other symmetry breaking

For certain models we have that $E_q - \epsilon = \epsilon - E_{q'}$ i.e. for some pairs $E_q + E_{q'} = 2\epsilon$ holds. This implies that
\[
\sum_{n=1}^{3}\lvert\Delta_n\rvert \left\{ \cos\left(\phi_n + \frac{\pi q n}{3}\right) + \cos\left(\phi_n + \frac{\pi q' n}{3}\right) \right\} = 0.
\]

Let $q = 1$ and $q' = 6$ (or $q = 2$, $q' = 5$; $q = 3$, $q' = 4$). We then have $q' + q = 1 \mod 6$. From here it follows that
\[
\sum_{n=1}^{3}\lvert\Delta_n\rvert \left\{ \cos\left(\frac{1 - q}{3}\pi n\right) + \phi_n + \cos\left(\frac{q' n}{3} + \phi_n\right) \right\} = 0
\]
for all $\Delta_n$, so equating the cosine arguments up to a difference of $\pi$ leads to $(q\pi n/3) = (q\pi n/3) \pm \pi$ or $2qn = n \pm 3$ for all $q$. Three cases arise depending on the number of neighbours entering the tight-binding model:

- If $n = 1$ (nearest neighbours), $2q\pi = -2\pi \mod 2\pi$ or $2q\pi = 4\pi$, valid for all $q$.
- If $n = 2$ (second neighbours), $4q\pi = 5\pi \mod 2\pi$ and there is no solution for $q$.
- If $n = 3$, $2q\pi = 0 \mod 2\pi$ for all $q$ and for both signs $\pm\pi$ considered above.

It is thus concluded from the second case that only second neighbours break the reflection symmetry of the spectrum around $\epsilon$ even when magnetic flux is introduced, while first and third neighbours preserve it.
2.4. Eigenfunctions and discrete currents

From the definition of current using our single electron Hamiltonian, we write
\[
\mathbf{j}(x) = \frac{\hbar}{m} \text{Im}(\psi^*(x) \hat{\nabla} \psi(x)) - \frac{e}{mc} A \psi^2
\]
\[
= \frac{\hbar}{m} \rho \nabla(S/h) - \left(\frac{e\rho}{mc}\right) A.
\]
(24)

However, in our discrete setting, we must re-derive the expression \( \mathbf{j} \) as a function of \( n \). Note that \( \mathbf{j} \) should always lie within the molecular plane. This, together with the eigenphases of \( C_6 \), suggests vorticity as explained in an experimental paper using electromagnetic waves [19]. A discrete version of the continuity equation is derived below using the tight-binding Hamiltonian (6) from which we can elucidate the discrete current term and the charge density; in our case they are related with the probability flux and the probability density \( |\psi|^2 \) respectively. We start from solutions of the time-dependent Schrödinger equation and its complex conjugate
\[
\psi^* \left( \frac{i\hbar}{\partial t} - H \right) \psi = 0, \quad \left( -i\hbar \frac{\partial}{\partial t} - H^* \right) \psi^* = 0.
\]
(25)

Upon addition we obtain
\[
i\hbar \frac{\partial}{\partial t} |\psi|^2 = \psi^* H \psi - \psi H^* \psi^*.
\]
(26)

In the discrete case an eigenstate of the system \( |\psi, t\rangle \) can be written as a linear combination of a complete basis \( \{|n\rangle\} \) of atomic states localised at the vertices of the hexagonal ring, thus we write
\[
|\psi, t\rangle = \sum_{n=1}^{6} \psi_n(t) |n\rangle
\]
and equation (26) can be re-expressed using the Hamiltonian (6) as follows, for each \( \psi_n \):
\[
i\hbar \frac{\partial}{\partial t} |\psi_n(t)|^2 = \psi_n^* \left[ \psi_n(t) + \sum_{k=1}^{3} (\Delta_k \psi_{n+k}(t) + \Delta_k^* \psi_{n-k}(t)) \right] - \psi_n(t) \left[ \psi_n^* \left( \frac{3}{k-1} \right) \left( \sum_{k=1}^{3} (\Delta_k \psi^*_{n+k}(t) + \Delta_k^* \psi^*_{n-k}(t)) \right) \right]
\]
\[
= \sum_{k=1}^{3} \left[ \Delta_k \psi_n^* \psi_{n+k}(t) + \Delta_k^* \psi_n^* \psi_{n-k}(t) \right] - \Delta_k^* \psi_n(t) \psi^*_{n+k}(t) - \Delta_k \psi_n(t) \psi^*_{n-k}(t).
\]
(28)

Assuming complex couplings \( \Delta_k \equiv |\Delta_k| e^{i\phi_k} \) to include the magnetic field, we have
\[
i\hbar \frac{\partial}{\partial t} |\psi_n(t)|^2 = \sum_{k=1}^{3} |\Delta_k| \left[ e^{i\phi_k} |\psi_n(t)\psi_{n+k}(t) - \psi_n(t)\psi_{n-k}(t)|^2 + e^{-i\phi_k} |\psi_n^*(t)\psi_{n-k}(t) - \psi_n^*(t)\psi_{n+k}(t)|^2 \right].
\]
(29)

It is important to mention at this point that our Hamiltonian is a Hermitian operator acting on a six dimensional Hilbert space and that the divergence theorem in a discrete setting must contain a sum over the ring sites. From equation (29) we may now verify

the discrete version of the continuity equation: upon summation over the sites \( n \), the l.h.s of (29) vanishes in the stationary case, i.e. conservation of probability
\[
i\hbar \sum_{n=1}^{6} \frac{\partial}{\partial t} |\psi_n(t)|^2 = i\hbar \frac{d}{dt} Q = 0
\]
(30)

where \( Q \) is the total probability. On the other hand the r.h.s of (29) vanishes by Hermiticity of the Hamiltonian; this is proved below
\[
i\hbar \sum_{n=1}^{6} \frac{\partial}{\partial t} |\psi_n(t)|^2 = \sum_{k=1}^{3} |\Delta_k| \left[ 6 \left( e^{i\phi_k} |\psi_n(t)\psi_{n+k}(t) - \psi_n(t)\psi_{n-k}(t)|^2 + e^{-i\phi_k} |\psi_n^*(t)\psi_{n-k}(t) - \psi_n^*(t)\psi_{n+k}(t)|^2 \right) \right]
\]
\[
= \sum_{n=1}^{3} \left( |\psi_n(t)|^2 |\psi_n^*(t)|^2 \psi_{n+k}^* \psi_{n-k}^* + |\psi_{n+k}(t)|^2 |\psi_{n-k}(t)|^2 \psi_n^* \psi_n \right)
\]
\[
= \sum_{n=1}^{3} \left( \psi_n H_{nm} \psi_{n+k} - \psi_n H_{nn} \psi_{n+k} \right),
\]
(31)

where we have taken \( \psi_n = |\psi_n| e^{i\theta_n} \). This indicates that the r.h.s. of (29) should be expressed as a current term of a discrete continuity equation
\[
i\hbar \sum_{k=1}^{3} \left( j_n^{(k)} - j_n^{(k)} \right) \alpha_k
\]
(32)

which always vanishes when
\[
\sum_{n=1}^{6} j_{n+k} = \sum_{n=1}^{6} j_n, \quad j_n = \sum_{k=1}^{3} j_n^{(k)}
\]
(33)

for \( k = 1, 2, 3 \) because of periodicity (mod 6). This is in full parallel with the divergence theorem. Some algebra must be done to find the exact expression for \( j_n^{(k)} \). Re-expressing the r.h.s. of (29)
\[
\sum_{k=1}^{3} \left[ |\Delta_k| \left( e^{i\phi_k} |\psi_n(t)\psi_{n+k}(t) - \psi_n(t)\psi_{n-k}(t)|^2 + e^{-i\phi_k} |\psi_n^*(t)\psi_{n-k}(t) - \psi_n^*(t)\psi_{n+k}(t)|^2 \right) \right]
\]
\[
= \sum_{k=1}^{3} \left( |\psi_n(t)|^2 |\psi_n^*(t)|^2 \psi_{n+k}^* \psi_{n-k}^* + |\psi_{n+k}(t)|^2 |\psi_{n-k}(t)|^2 \psi_n^* \psi_n \right)
\]
\[
= \sum_{n=1}^{3} \left( \psi_n H_{nm} \psi_{n+k} - \psi_n H_{nn} \psi_{n+k} \right)
\]
(34)

we note that it coincides with (32) if
\[
|\Delta_k| = \alpha_k \quad \text{and} \quad j_n^{(k)} = \frac{1}{i\hbar} \left( e^{i\phi_k} \psi_n \psi_{n+k} - e^{-i\phi_k} \psi_{n-k} \psi_{n+k} \right)
\]
\[
= \frac{2}{i\hbar} \text{Im}(e^{i\phi_k} \psi_n \psi_{n+k}).
\]
(35)

For eigenfunctions, we trivially recover
\[
\frac{\partial}{\partial t} (|\psi_n(t)|^2) = 0 \quad \text{and} \quad \sum_{k=1}^{3} (j_{n+k}^{(k)} - j_n^{(k)}) \alpha_k = 0.
\]
(36)

Now we can write the stationary wave function as \( \psi_n(t) = \psi_n e^{-i\phi_n t/\hbar} \) in order to obtain an expression for the
This represents a stationary current related to $k$ neighbours. The currents are plotted in figure 4 (benzene) and figure 5 (borazine) for the particular case of nearest neighbours ($k = 1$) and $\varphi_n \in \mathbb{R}$. The length of the arrow lines represent the intensity of the current. The maximum value is reached when the phase is $\phi = \pi/2$.

2.5. Numerical results

This section presents some calculations for benzene. The necessary data, such as valence energy, atomic distances and bond angles are well-known and reported in several handbooks and articles [35, 38, 39]. Since we are only interested in the distance dependence of the couplings, we focus our interest in the radial part of the atomic wave function. Regarding the molecular structure and the well-known bonding structure in benzene as a reasonable estimate, we restrict ourselves to the $p_z$ orbital. The radial dependence of $p_z$ has the following form:

$$R(r) = A r^{-\lambda} e^{-r/\lambda}, \quad \lambda = \frac{2a_0}{Z}, \quad A = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Z}{\sqrt{3}a_0}.$$  \hspace{1cm} (38)

where $a_0$ stands for the Bohr radius and $Z$ for the nuclear charge. The couplings are given by the overlap integral in equation (3). A reasonable approximation of the wave function in regions outside the atom is $R(r) \sim e^{-r/\lambda}$, therefore the couplings take the form

$$\Delta \sim \Delta_0 e^{-d/\lambda}, \quad \lambda = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2},$$  \hspace{1cm} (39)

where $d$ is the distance between the two atoms; $\lambda_1$ and $\lambda_2$ are the evanescence lengths for atoms 1 and 2 correspondingly and $\Delta_0$ is a constant. For benzene $\lambda_C = a_0/3$ and in order to obtain numerical values of $\Delta_0$ and site energies, we may take the information from parameters of graphene [35, 39].

Figure 6 shows the resulting energy levels obtained from our model and the spectrum of graphene was included for visual reference. Panel (a) illustrates a first neighbour coupling spectrum where the up–down symmetry is present; on the other hand, panel (b) shows the spectrum of benzene including second neighbours, where the up–down symmetry is visibly broken. Panel (c) corresponds to the full spectrum.

Figure 4. Current plots for the six eigenfunctions of the benzene molecule under the action of a magnetic field of $B = 8.5855 \times 10^{-3}$ G perpendicular to the ring plane. Note that the superior and inferior rows correspond to reflected energy levels, the only way to distinguish between them is the current scheme. Panels (a) and (d) correspond to singlet states. Panels (b), (c) and (e), (f) show the inequivalent current schemes for the superior and inferior lifted doublets respectively. It is worth noting that both rows are inverted current schemes of each other.

5 Other corrections to the Bohr radius may arise from the atomic shielding, which modifies the evanescence length of the wave function [40, 41]. Nevertheless, for the purpose of the present work, this does not introduce major corrections and can be dismissed.
with all pairwise couplings. The corrections to the level structure generated by third neighbour couplings are not quantitatively relevant and we may conclude that a nearest neighbour model suffices for the description of the benzene ring. Panels (d), (e) and (f) illustrate the level splitting of doublets in three different ways:

(i) Introducing a defect in one site. See panel (d) of figure 6.
(ii) Introducing coupling defects in \( \Delta_{(1,2)} \), \( \Delta_{(1,6)} \), \( \Delta_{(2,1)} \) and \( \Delta_{(6,1)} \). Figure 6 panel (e).
(iii) Introducing a magnetic field through the benzene ring. See panel (f) of figure 6.

The eigenfunctions are plotted in figure 7 for a nearest neighbour model and for the one-site defect Hamiltonian in figure 8. A ring is shown as a visual reference. This numerical analysis is presented for borazine at the end of section 3.

In artificial realisations, the evanescence length \( \lambda \) can be obtained from previous knowledge of localised states at discs, corners or junctions. An interesting case arises when \( \lambda \) is comparable to the bonding length where a triple degeneracy point was found in a second neighbour coupling model when \( \Delta_2/\Delta_1 = 1/3 \), as illustrated in panel (a) of figure 9. Moreover, a level inversion between inferior doublet and singlet when \( \Delta_2/\Delta_1 > 1/3 \) is presented in panel (b) of figure 9. In the third neighbour coupling model, the triple degeneracy point emerges when \( 1 - 3(\Delta_2/\Delta_1) + 4(\Delta_3/\Delta_1) = 0 \). This doublet–singlet degeneracy has been studied previously by means of geometric deformations [17].

3. Borazine

3.1. Multiple neighbours in a \( C_3 \) scheme

In this section we introduce a system with only a (partial) triangular symmetry, in contrast with benzene, as it is the appropriate model for a borazine molecule. The group \( C_3 \) can be decomposed into \( C_1 \) and \( C_2 \): \( C_2 = C_1 \times C_1 = \left\{ 1, \tau, \tau^2 \right\} \times \left\{ 1, P \right\} \), such that \( P^2 = 1 \) and \( \tau^3 = 1 \). Evidently \( T^2 = \tau \), as it represents a rotation of \( 2\pi/3 \) radians around the centre of a hexagon, and \( P \) swaps boron and nitrogen sites. Only N (nitrogen) centres allow shuffling; similarly, only B (boron) centres allow shuffling among themselves. The on-site energies for valence orbitals are different: \( E_B = \epsilon_1 \), \( E_N = \epsilon_2 \). As for the couplings, the \( C_3 \) symmetry is preserved if \( \Delta_1 \) represents N–B couplings (nearest neighbours), \( \Delta_2 \) represents either B–B couplings (\( \Delta_2^* \)) or N–N couplings (\( \Delta_2 \)) and \( \Delta_3 \) yields the N–B couplings between opposite vertices, which must be identical in

Figure 5. Current plots for the eigenfunctions of the borazine molecule under a magnetic field of \( B = 8.5855 \times 10^{-3} \) G. Similarly to the benzene case, the singlets of panels (a) and (d) show opposite current directions. Panels (b), (c) and (e), (f) correspond to the lifted doublets states. The current schemes are different and make a distinction between reflected energy levels.
all three possibilities according to the geometry. The resulting Hamiltonian is reorganised as

\[
H = \begin{pmatrix}
\epsilon_1 & \Delta_1^+ & \Delta_2^+ & \Delta_3 & \Delta_4 & \Delta_5 \\
\Delta_1^+ & \epsilon_1 & \Delta_2 & \Delta_3 & \Delta_4 & \Delta_5 \\
\Delta_2^+ & \Delta_1 & \epsilon_2 & \Delta_2 & \Delta_4 & \Delta_5 \\
\Delta_3 & \Delta_1 & \Delta_2 & \epsilon_1 & \Delta_4 & \Delta_5 \\
\Delta_4 & \Delta_1 & \Delta_2 & \Delta_3 & \epsilon_2 & \Delta_5 \\
\Delta_5 & \Delta_1 & \Delta_2 & \Delta_3 & \Delta_4 & \epsilon_2
\end{pmatrix}
\]

The operation \( P[N] = |B\rangle \), \( P[B] = |N\rangle \) in its matrix form is represented by

\[
P = \begin{pmatrix}
0 & I_{3 \times 3} & 0 \\
I_{3 \times 3} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

\( \otimes \sigma_1 \).

Figure 6. Energy levels of benzene. The distance between sites is taken as 1.39 Å and the on-site energy is shifted to 0. The dispersion relation of graphene is included to guide the eye; a sketch of the Brillouin zone is included in the top panel. (a) Nearest-neighbour couplings. The energy structure (from top to bottom) is singlet, doublet, doublet, singlet. The energy levels possess a reflection symmetry. (b) Second neighbour couplings break reflection symmetry. (c) Third nearest-neighbour couplings. The corrections to energy levels due to second and third neighbours are negligible. (d) Nearest neighbour couplings with a site defect of 1 eV. (e) Nearest neighbour couplings with coupling defects (1, 2), (1, 6), (6, 1) and (2, 1) by 0.3 eV. (f) Nearest neighbour couplings with external magnetic field perpendicular to the ring plane of \( B = 8.5855 \times 10^{-3} \) G. The dashed lines correspond to the graphene spectrum obtained from a nearest-neighbour tight-binding model.

where \( \sigma_i \) stands for the Pauli matrices. Now the matrix representation of the translation operator \( \tau \) in \( C_3 \) is

\[
\tau |N_k\rangle = |N_{(k+1) \text{mod } 3}\rangle, \quad \tau |B_k\rangle = |B_{(k+1) \text{mod } 3}\rangle,
\]

\[
\tau = \begin{pmatrix}
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\]

\( \otimes I_{2 \times 2} \).

Let us introduce the notation \(|n, m\rangle\) for the localised states, where \( n \) represents the number of subtriangles (1 for boron and 2 for nitrogen) and the index \( m \) represents the internal position in each subtriangle. In this notation, \( P \) and \( \tau \) operate as follows

\[
P |n, m\rangle = |(n + 1) \text{mod } 2, m\rangle,
\]

\[
\tau |n, m\rangle = |n, (m + 1) \text{mod } 3\rangle,
\]

\( [\tau, P] = 0 \).
Figure 7. Eigenfunctions for a nearest neighbour tight-binding model of benzene. Panels (a) and (d) represent the singlet states and display the same probability of finding the electron in any of the six sites of the ring. The benzene ring is presented as a visual reference of the spatial dependence of the eigenfunctions.

Figure 8. Eigenfunctions of a benzene ring with $C_6$ symmetry broken by one site defect of 1 eV. The spectrum is depicted in panel (d) of figure 4. Panels (a) and (d) show singlet eigenfunctions, the probability is modified in the region around the defect site. Panels (b) and (e) depict that the modification to the probability is presented in two sites of the ring, while in panels (c) and (f) no visual change is present.
The Hamiltonian must be expressed as a sum of operators, therefore we need to define other matrices:

\[ Q_\pm = I_{3 \times 3} \otimes \sigma_\pm \quad \text{and} \quad \Pi_\pm = I_{3 \times 3} \otimes (1/2)(I_{2 \times 2} \pm \sigma_3), \]

(44)

where \( \sigma_\pm = (1/2)(\sigma_1 \pm i\sigma_2) \). \( H \) can be expressed now as function of the operators \( \Pi_\pm, \tau \) and \( Q_\pm \):

\[
H = \Pi_+ (\epsilon_1 + \tau \Delta_1^+ + \tau^* \Delta_1^-) + \Pi_- (\epsilon_2 + \tau \Delta_2^- + \tau^* \Delta_2^+) + Q_1 (\Delta_1 + \Delta_1^\tau + \Delta_1^\tau \tau) + Q_2 (\Delta_2 + \Delta_2^\tau + \Delta_2^\tau \tau),
\]

(45)

with the following commutation and anticommutation relations

\[
\{Q_\pm, Q_{\pm'}\} = 0, \quad \{Q_{\pm}, \tau^n\} = 0, \quad \{\Pi_{\pm}, \tau\} = 0
\]

\[
\{Q_+, Q_-\} = I_{3 \times 3} \otimes [\sigma_+ , \sigma_-] = I_{3 \times 3} \otimes \sigma_3 = \Pi_+ - \Pi_- = \Sigma_3
\]

\[
\{Q_{\pm}, \Pi_{\pm}\} = I_{3 \times 3} \otimes [\sigma_+ , \sigma_-] = \Pi_+ + \Pi_- = I_{6 \times 6}
\]

\[
\{Q_\pm, \Pi_{\pm}\} = I_{3 \times 3} \otimes [\sigma_- , (I_{2 \times 2} \pm \sigma_3)/2] = I_{3 \times 3} \otimes \sigma_- = Q_\pm.
\]

(46)

This problem can be happily solved in a simple way by using the eigenphases of \( C_3 \), which turn out to be

\[
|l\rangle = \frac{1}{\sqrt{2}} \sum_{m=-1}^{3} e^{-i\frac{\pi}{3}m} |n, m\rangle, \quad l = 1, 2, 3
\]

\[
|l, n\rangle = \frac{1}{\sqrt{3}} \sum_{m=1}^{3} e^{-i\frac{\pi}{3}m} |n, m\rangle, \quad \langle l', n'|l, n\rangle = \delta_{nn'} \delta_{ll'}
\]

(47)

The elements of the basis \( \{|l\rangle\} \) are eigenstates of the translation operator \( \tau \):

\[
\tau |l\rangle = e^{i2\pi l} |l\rangle, \quad l = 1, 2, 3.
\]

(48)

The Hamiltonian operates on \( |l\rangle \) as below

\[
H|l\rangle = \left\{ \Pi_+ \left[ \epsilon_1 + 2\Delta_1^\tau \cos \left( \frac{2\pi l}{3} \right) \right] + \Pi_- \left[ \epsilon_2 + 2\Delta_2^\tau \cos \left( \frac{2\pi l}{3} \right) \right] + Q_1 (\Delta_1 + \Delta_1^\tau\tau + \Delta_1^\tau \tau) + Q_2 (\Delta_2 + \Delta_2^\tau \tau + \Delta_2^\tau \tau) \right\} |l\rangle.
\]

(49)

Now, the operators \( Q_\pm \) and \( \Pi_\pm \) acting on \( |l\rangle \) result in the following

\[
\Pi_+ |l\rangle = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{2}} \sum_{m=1}^{3} e^{i\frac{\pi}{3}m} |1, m\rangle = \sqrt{2} |l, 1\rangle
\]

\[
\Pi_- |l\rangle = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{2}} \sum_{m=1}^{3} e^{i\frac{\pi}{3}m} |2, m\rangle = \sqrt{2} |l, 2\rangle
\]

\[
Q_+ |l\rangle = \sqrt{2} |l, 1\rangle
\]

\[
Q_- |l\rangle = \sqrt{2} |l, 2\rangle
\]

\[
\tau |l, n\rangle = e^{i2\pi l} |l, n\rangle.
\]

(50)

Finally, the Hamiltonian operates on \( \{|l, n\rangle\} \) as

\[
H|l, l\rangle = \left[ \epsilon_1 + 2\Delta_1^\tau \cos \left( \frac{2\pi l}{3} \right) \right] |l, 1\rangle
\]

\[
+ [\Delta_1 + \Delta_1^\tau e^{-i\frac{\pi}{3}} + \Delta_2 e^{i\frac{\pi}{3}}] |l, 2\rangle
\]

(51)

leading to the following matrix representation:

\[
H_{11} = \begin{bmatrix}
\epsilon_1 + 2\Delta_1^\tau \cos \left( \frac{2\pi l}{3} \right) & \Delta_1 + \Delta_1^\tau e^{-i\frac{\pi}{3}} + \Delta_2 e^{i\frac{\pi}{3}} \\
\Delta_1 + \Delta_2 e^{i\frac{\pi}{3}} + \Delta_1^\tau e^{-i\frac{\pi}{3}} & \epsilon_2 + 2\Delta_2^\tau \cos \left( \frac{2\pi l}{3} \right)
\end{bmatrix}
\]

(52)

where \( l = 1, 2, 3 \) and which is solvable by radicals. The wave functions are explicitly given by

\[
N^{(l)} |l, 1\rangle - A^{(l)} |l, 2\rangle, \quad N^{(l)} |l, 1\rangle + (A^{(l)})^* |l, 2\rangle.
\]

(53)

where, in terms of matrix elements \( H_{ij}^{(l)} \) above, we write

\[
N^{(l)} = \frac{1}{\sqrt{1 + |A^{(l)}|^2}},
\]

\[
A^{(l)} = \frac{H_{12}^{(l)}}{2} + \sqrt{\left( \frac{H_{12}^{(l)}}{2} \right)^2 + H_{12}^{(l)2}}.
\]

(54)

These expressions can be regarded as analytical solutions which, to our knowledge, have not been provided for borazine elsewhere.

### 3.2. Numerical results

Now we analyse the numerical results for the borazine molecule using the method described in section 2. The on-site energies and other geometric parameters of the molecule can be found in \([34, 38, 42, 43]\). The evanescence lengths for N and B are \( \lambda_N = 2a_0/7 \) and \( \lambda_B = 2a_0/5 \) respectively. The coupling \( \Delta_0 \) is obtained from the band width of the dispersion relation for boron nitride.

The spectrum of band borazine is depicted in figure 10 together with the dispersion relation of boron nitride as reference.
Panels (a), (b) and (c) correspond to nearest-neighbour, second-neighbour and third-neighbour models respectively. Corrections due to the incorporation of all pairwise couplings are negligible compared to the nearest-neighbour case. The second row of figure 10 shows doublet splitting via introduction of one defect, panel (d); coupling defects in $\Delta_{1,6}$, $\Delta_{2,1}$ and $\Delta_{6,1}$, panel (e); introduction of a magnetic field perpendicular to the borazine ring, panel (f). The eigenfunctions are plotted in figure 11 for nearest-neighbour borazine and in figure 12 for borazine with broken $C_3$ symmetry.

4. Supersymmetry

The two copies of a triangle spectrum that appear reflected in benzene and borazine can be explained by finding the dynamical SUSY of the ring. For the Dirac oscillator, the supersymmetry is well-known, as the reader may verify in [18, 44]. In our present case, a similar treatment can be developed in order to define a superalgebra. Let us rewrite the Hamiltonian (45) as follows:

$$H = \hat{\Pi}_+ (\epsilon_1 + \tau \Delta^+_2 + \tau^\dagger \Delta^+_3) + \hat{\Pi}_- (\epsilon_2 + \tau \Delta^-_2 + \tau^\dagger \Delta^-_3) + \hat{C}_i$$

where the operators $\hat{C}_i$, $\hat{\epsilon}_0$ and $\hat{\mu}$ have been defined as

$$\hat{C}_i = Q_+ (\Delta_1 + \Delta^\tau + \Delta^\tau_3) + Q_- (\Delta_1 + \Delta^\tau + \Delta^\tau_3)$$

$$\hat{\epsilon}_0 = \frac{1}{2} [ (\epsilon_1 + \epsilon_2) I_{6 \times 6} + \tau \Delta^+_2 + \tau^\dagger \Delta^+_3 + \tau \Delta^-_2 + \tau^\dagger \Delta^-_3]$$

$$\hat{\mu} = \frac{1}{2} [ (\epsilon_1 - \epsilon_2) I_{6 \times 6} + \tau \Delta^+_2 + \tau^\dagger \Delta^+_3 + \tau^\tau_2 - \tau \Delta^-_3 - \tau^\dagger \Delta^-_3]$$.

(56)

Following [18] we define the operator $\hat{C}_2$ as:

$$\hat{C}_2 = -iQ_+ \hat{a} + iQ_- \hat{a}^\dagger$$.

(57)

and the ‘bosonic’ definitions of $a$ and $a^\dagger$ are shown below:

$$\hat{a} = \Delta_1 + \Delta^\tau + \Delta^\tau_3$$

$$\hat{a}^\dagger = \Delta_1 + \Delta^\tau + \Delta^\tau_3$$.

(58)

We verify the (anti)commutation relations between $\hat{C}_i$ and $\hat{\mu}_{\Sigma}$

$$\{ \hat{C}_i, \hat{\mu}_{\Sigma} \} = 0$$

$$\{ \hat{\mu}_{\Sigma}, \hat{\mu}_{\Sigma} \} = 0$$

$$\{ \hat{\mu}_{\Sigma}, \hat{\mu}_{\Sigma} \} = 0$$.

(59)

Now, if we have that $\hat{a}$ and $\hat{\mu}$ commute, a central charge $(H - \hat{\epsilon}_0)^2 - \hat{\mu}^2$ can be defined and the following SUSY is
Since this $S(2)$ superalgebra is dynamical, we do not expect the charges $C_{1,2}$ to relate bosonic and fermionic sectors directly. Instead, they connect energy states below the central level (here taken as $\epsilon = 0$) with those above. In a general sense, the supercharges relate dressed states, made of dimers and trimers. When we look for the operators that relate undressed bosonic and fermionic sectors, we encounter $Q_{\pm}$ as responsible for such operation. In particular, $a, a'$ are an Abelian realisation of ladder operators that are admissible in our finite $3 \times 3$ representation, while $\Sigma_i$ constitutes the undressed fermionic sector, as obviously shown by $\{\Sigma_i, \Sigma_j\} = 2\delta_{ij}1_{4\times 4}$. Some interesting consequences can be studied from the model above:

- If $[\hat{\mu}, a] \neq 0$ (and as a consequence $[\hat{\mu}, a'] \neq 0$) then the relation $\{\hat{C}_i, \hat{C}_j\} = 2\delta_{ij}[(H - \hat{\epsilon}_0)^2 - \hat{\mu}^2]$ breaks and the term $(H - \hat{\epsilon}_0)^2 - \hat{\mu}^2$ cannot be used as the central charge any more, thereby breaking the SUSY.

- If $[\hat{\mu}, a'] = 0$ (Heisenberg and other Cartan algebras, for example) the dynamical SUSY is preserved.

For each subtriangle, if the symmetry group $C_3$ holds then $\hat{\mu} \propto 1$ and $[\hat{\mu}, a] = 0$, but if we have intertriangular couplings that break $C_3$ globally, then $[\hat{\mu}, a'] \neq 0$ in general. The supersymmetry is preserved even if we break the global $C_3$, but not the symmetry of each subtriangle.

Due to $(H - \hat{\epsilon}_0)^2 - \hat{\mu}^2$, the dynamical SUSY yields reflection symmetry between energy pairs with variable
Figure 11. Eigenfunctions for a nearest neighbour tight-binding model of borazine. Yellow spheres represent nitrogen atoms and green boron atoms. Panels (a) and (d) show the singlet states. Panels (b), (c) and (e), (f) show the wave functions for degenerated doublets.

Figure 12. Eigenfunctions of borazine ring with $C_3$ symmetry broken by one site defect increment of 0.7 eV. Yellow spheres represent nitrogen atoms, green boron and the black spheres is for the on-site defect. Panels (a) and (d) stand for the singlet levels. Panels (b), (c) and (e), (f) illustrate the wave functions of the lifted doublets.
geometric centres according to $l = 1, 2, 3$. Such centres add to $3(e_1 + e_2) / 2$ always. Since $C_3$ is not broken in benzene or borazine, we may conclude that these compounds enjoy SUSY in their spectrum.

It is interesting to note that a generalisation of the algebra (60) to deformed cases might be helpful to deal with asymmetrical configurations of the molecule, say, if external strain or vibrations are applied to it. In this scenario, the $C_3$ sector is no longer valid. In addition, the typical bosonic promotion $[a, a^\dagger] = 1$ does not work in finite dimension because the Heisenberg algebra is non-compact. The possibilities that can be considered here are the Cartan forms of compact algebras such as $J_{\pm}$ for $su(2)$ for $j = 1$ or hypercharge operators $U_{\pm}$, $V_{\pm}$ for one of the fundamental irreps of $su(3)$.

5. Conclusion

The electronic structure of benzene and borazine was studied with the tight-binding formalism. Nearest neighbours dominate the shape of the electronic levels with the appropriate values of evanescence lengths for all type of atoms. Theoretical models with dominating second-neighbour couplings were explored. The resulting spectra turned out to be asymmetric and in the extreme situation where the evanescence length is comparable to the bond length between nearest neighbours, a triplet state was found or doublet–singlet inversions could be produced. The discrete version of the continuity equation and discrete current descriptions of fluorescence length is comparable to the bond length between benzene or borazine. With algebraic techniques, we were able to extract the most salient features of homogeneous and composite hexagonal rings. Moreover, the existence of a supersymmetry was found, explaining the up–down symmetry of the energy levels, and in more refined cases a sum rule of energy midpoints.

Interestingly, the generality of our results can be used to propose the construction of artificial realisations in micro-waves [20–23] and elastic vibrations [24–26]. The latter are supported by recent engineering of evanescent couplings in solids [45–47], much in the spirit of quantum tunnelling.

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