Non-perturbative magnetic phenomena in closed-shell paramagnetic molecules

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By means of non-perturbative ab initio calculations, it is shown that paramagnetic closed-shell molecules are characterized by a strongly non-linear magnetic response, whose main feature consists of a paramagnetic-to-diamagnetic transition in a strong magnetic field. The physical origin of this phenomenon is rationalised on the basis of an analytical model based on molecular orbital theory. For the largest molecules considered here, the acepleiadylene dianion and the corannulene dianion, the transition field is of the order of 10^3 T, about one order of magnitude larger than the magnetic field strength currently achievable in experimental settings. However, our simple model suggests that the paramagnetic-to-diamagnetic transition is a universal property of paramagnetic closed-shell systems in strong magnetic fields, provided no singlet–triplet level crossing occurs for fields smaller than the critical transition field. Accordingly, fields weaker than 100 T should suffice to trigger the predicted transition for systems whose size is still well within the (medium–large) molecular domain, such as hypothetical antiaromatic rings with less than one hundred carbon atoms.

I. Introduction

The full ab initio characterisation of closed-shell molecules interacting with external uniform magnetic fields has mostly been based on the assumption that the molecular energy \( W(\mathbf{B}) \) as a function of magnetic field \( \mathbf{B} \) can be approximated in terms of a rapidly convergent polynomial expansion given by (Einstein summation convention)

\[
W(\mathbf{B}) = W(0) + \frac{1}{2} \sum_{\alpha \beta} B_{\alpha} B_{\beta} \chi_{\alpha \beta} + \frac{1}{4!} \sum_{\alpha \beta \gamma \delta} B_{\alpha} B_{\beta} B_{\gamma} B_{\delta} \chi_{\alpha \beta \gamma \delta} + \cdots
\]

where \( W(0) \) is the molecular energy in zero-field, \( \chi_{\alpha \beta} \) is the second-rank magnetisability and \( \chi_{\alpha \beta \gamma \delta} \) is the fourth-rank hypermagnetisability. Since the magnetic interaction energy is proportional to the magnetic flux—that is, to the product between the external field strength and the area of the perpendicular molecular surface—the polynomial ansatz is clearly a very good one for small molecules subject to experimentally achievable magnetic fields, which at best can be of the order of 10^2 T.\(^1\)

However, with the recent progress in computational techniques, ab initio quantum chemistry is nowadays expanding its traditional domain of interest to larger systems. For such systems, the effect of a magnetic field of a few tens of tesla can, in principle, and in a non-negligible way, change the very nature of the molecular wave function, with important observable consequences. Indicative examples are the semiconductor-to-metal transition in carbon nanotubes caused by a strong field along their axes\(^2,3\) and the very recent observation of room-temperature quantum-Hall effect in diamagnetic graphene sheets.\(^4\) In the literature, a few studies have appeared concerning the perturbative calculation of fourth-rank hypermagnetisabilities,\(^5,6\) the induced non-linear ring current in aromatic and antiaromatic molecules,\(^7\) and the electric\(^8\) and magnetic\(^9,10\) hypershieldings at the nuclei. However, apart from work on atoms and very small molecules such as H\(_2\) (see ref. 11 and references therein), to the best of our knowledge, the only quantum-chemical ab initio investigation of the non-perturbative behaviour of closed-shell molecules in strong magnetic fields was reported in ref. 12 by the present authors.

One well-known problem affecting the convergence of finite-basis ab initio calculations of magnetic properties is the gauge-origin dependence of the results and the associated slow basis-set convergence of the calculated properties. Many techniques have been proposed to solve this problem, the most efficient one being based on the use of London orbitals.\(^13-15\) Unfortunately, none of these techniques is straightforwardly applicable to finite-field calculations. Recently, we presented a scheme for the use of London orbitals with magnetic fields of arbitrary strength\(^12\) and implemented this scheme in the program LONDON,\(^16\) providing a gauge-origin invariant approach to non-perturbative restricted Hartree-Fock (RHF) self-consistent field (SCF) molecular calculations in strong magnetic fields.

The purpose of the present paper is to demonstrate, by means of gauge-origin invariant non-perturbative SCF calculations, a very simple paradigm: due to strongly non-linear effects, closed-shell paramagnetic systems become diamagnetic in high magnetic fields. We show here that the
perturbative approach based on eqn (1.1) is of little use for describing these strong non-linearities and that, instead, non-perturbative methods become necessary. We note here that interesting magnetic behaviours are always associated with quasi-degeneracies in the electronic spectrum, so that a multi-reference treatment would be more appropriate for making quantitative predictions. However, only the SCF approach presented in ref. 12 is available for the time being and, especially for the closed-shell systems considered here, the qualitative features captured by SCF are expected to survive more accurate approaches accounting for non-dynamic as well as dynamic correlation. Consequently, all calculations presented in this paper have been carried out at the RHF level of theory. We also limit our study to purely electronic effects, since our present methodology does not allow us to study the effect of strong magnetic fields on molecular structure in general. In this work, magnetic fields are expressed in atomic units (a.u.) of magnetic flux density. Conversion to SI units (T) is readily given by $1 \text{ a.u.} = \frac{h}{e^2} \frac{1}{\text{a.m.u.}} = 2.35 \times 10^5 \text{T}$.

Hints of the strong magnetic non-linearity implied by closed-shell paramagnetism were already given in previous works. In this study, those preliminary statements are confirmed for a whole range of paramagnetic closed-shell systems. Moreover, a rationalization of the underlying physics is provided on the basis of a simple analytical model.

II. Ab initio non-linear response of closed-shell paramagnetic systems

It is well known that paramagnetism is, in most cases, a temperature-dependent phenomenon, originating from the unpaired electrons of an open-shell species. However, as early as in the beginning of the last century, a number of closed-shell substances were found to have a paramagnetic susceptibility quite independent of the temperature, one of the earliest examples being the permanganate ion, MnO$_4^-$. A general theory (for closed- and open-shell systems) of temperature-independent paramagnetism in the weak-field limit was first introduced by van Vleck. At first, the theory for paramagnetism of closed-shell molecules was challenged by a theorem proving that the magnetizability of closed-shell systems is always negative, arguing on the basis of a gauge transformation designed to annihilate the paramagnetic contribution to the total magnetizability. However, a fundamental flaw in the proof was later discovered by Hegstrom and Lipscomb, who confined the validity of the gauge transformation (thus of the theorem) to systems with less than four electrons. Hence, closed-shell molecules with at least four electrons can, in principle, be paramagnetic in the spirit of van Vleck.

We consider here three main classes of systems displaying some degree of closed-shell paramagnetism (see Fig. 1) and investigate their response to strong magnetic fields using the ab initio package LONDON. The first class consists of well-known small paramagnetic molecules such as the hydrides BH$_1$ and CH$^+$ and the anion MnO$_4^-$. The second class consists of planar [4n]-carbocycles. As is well known, the linear magnetic response of these systems is characterized by paramagnetic ring currents due to π-electrons, which may or may not result in global closed-shell paramagnetism.

According to a widely accepted definition of aromaticity and antiaromaticity based on the magnetic criterion, such systems are here referred to as antiaromatic. Examples of experimentally characterised antiaromatic planar [4n]-carbocycles are clamped cyclo-octatetraene (COT, $n = 2$), fully annelated both with perfluorocyclobuteno groups, with bicyclo[2.1.1]-hexene groups, and the dehydro[12]-annulene ($n = 3$) fused with bicyclo[2.2.2]octane frameworks, for which NMR measurements confirmed the existence of a paramagnetic ring current. We here consider the first three members of the [4n]-carbocycles series, which represent ab initio models for the conjugated planar moieties of the synthetic molecules: cyclobutadiene ($n = 1$), COT ($n = 2$) and [12]-annulene ($n = 3$). Finally, we consider two organic diamions that have been experimentally and computationally characterized as closed-shell paramagnetic systems: the acepleiadylene dianon C$_{16}$H$_{10}^2-$, and the corannulene dianon C$_{20}$H$_{12}^2$-Unless otherwise stated, all geometries were optimized at the RHF/6-31G** level of theory, imposing planarity to the annulene structures to mimic the electronic structure of the above-mentioned synthetic molecules.

A. Small molecules

Several ab initio computational studies have been reported on the magnetic properties of BH, CH$^+$ and MnO$_4^-$. At all levels of theory, previous investigations on these systems concur in finding their linear magnetizability to be positive, characterising them as closed-shell paramagnetic molecules. For BH and CH$^+$, the component of the magnetizability...
perpendicular to the bond is paramagnetic, and large enough to dominate the average response. To the best of our knowledge, no investigation of the response of these systems to strong fields has appeared in the literature, with the exception of a preliminary study on BH that we reported in a recent work as a test case for our new methodology.\textsuperscript{12}

In particular, in ref. 12 we found that the energy of BH as a function of field presents a non-trivial behaviour that cannot be easily reproduced by the expansion in eqn (1.1). The energy versus field curve for BH has in fact a sombrero shape, with minimum at \( B \approx \pm 0.22 \) a.u. The field strength defining the energy minimum characterises the transition of the system from closed-shell paramagnetic to closed-shell diamagnetic. This follows from the slope of the energy curve changed by sign, which defines the total magnetic moment induced in the system. In fact, the slope is negative before the transition field, defining an induced magnetic moment parallel to the external field—that is, a paramagnetic state. At the energy minimum the slope is zero, characterising a state in which the induced orbital magnetic moment is completely quenched. Beyond the transition field, the induced magnetic moment opposes the external perturbation (positive slope), the signature of a diamagnetic system. The basic question addressed in the present work is thus whether the strongly non-linear behaviour leading to a paramagnetic-to-diamagnetic transition observed for BH is common to all paramagnetic closed-shell systems and, if so, what is its underlying physical origin. In Fig. 2, we have plotted the RHF ground-state energy against the magnetic field for a series of London basis sets of increasing quality, for BH, CH\textsuperscript{+} and MnO\textsuperscript{4-}. Whereas the largest basis for BH and CH\textsuperscript{+} is aug-cc-pVDZ for both atoms, the largest MnO\textsuperscript{4-} basis consists of an uncontracted Wachters + f basis\textsuperscript{35,36} on the Mn centre and aug-cc-pVDZ on the oxygen atoms.

As is evident from Fig. 2, the features previously reported for the energy versus field diagram of BH are observed for all systems. The energy lowers when the field is switched on, it reaches a minimum, and then raises again, displaying a typical behavior of a paramagnetic (diamagnetic) system for very low (high) fields. The details of the plots clearly depend on the specific system and the basis set employed. In particular, we notice that, for the largest basis sets used here, the critical field, \( B_c \), at the energy minimum for BH, CH\textsuperscript{+} and MnO\textsuperscript{4-} is found at 0.23, 0.45 and 0.50 a.u., respectively.

However, it is important to note that, for such high fields, the first triplet excited state also lowers its energy by the pure spin-Zeeman interaction, so that the energy spectrum could, in principle, display level crossing (LC) for \( B < B_c \). To check this possibility, let \( W_{S,M_S}(B) \) denote the energy of the \((S,M_S)\) level at field strength \( B \) and denote by \( \Delta W_T = W_{1,-1}(0) - W_{0,0}(0) \) the triplet excitation energy at zero field. Neglecting spin–orbit coupling and orbital effects on the triplet state, we then estimate that the level crossing occurs at the field strength \( B_{LC} \) given by

\[
W_{0,0}(B_{LC}) = W_{1,-1}(B_{LC}) = W_{0,0}(0) + \Delta W_T - g\mu_B B_{LC}.
\]

(2.2)

where the isotropic g-factor is given by \( g = 2 \) and the Bohr magneton by \( \mu_B = 1/2 \) a.u. Computing the lowest triplet

![Fig. 2 Plots of the ground state HF energy variation (\( E_0 \)) as a function of the external magnetic field (atomic units of magnetic flux density, \( hc^{-1}a_0^2 = 2.35 \times 10^5 \) T) for (a) BH, (b) CH\textsuperscript{+}, and (c) MnO\textsuperscript{4-}. The diagrams are calculated using a series of uncontracted basis sets of increasing quality (see text, and the figure legends), all augmented with London gauge factors.](image-url)

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**B Antiaromatic closed-shell carboycles**

In this work, we investigate three systems belonging to the antiaromatic [4\textit{n}]-carboycle series: cyclobutadiene (\( n = 1 \)), flattened cyclo-octatetraene, and [12]-annulene. The results of the finite-field calculations are plotted in Fig. 3.
Cyclobutadiene represents the only system of the series that is globally diamagnetic. Even though it is characterised by a paramagnetic response of its $\pi$ electrons, this response is counterbalanced and overwhelmed by the localized diamagnetic response of the $\sigma$ framework. However, as discussed in ref. 12, the energy versus field curve for this system presents marked features of strong non-linearity, in agreement with the fact that its $\pi$-electron states can be viewed as a closed-shell paramagnetic subsystem.

Because of the separability of the $\sigma$–$\pi$ one-electron states based on symmetry, it is possible to plot an estimate of the $\pi$-electron energy as function of field, approximating it by the sum of the $\pi$-electron orbital energies. The results are reported in Fig. 3b, where we can see that the pure closed-shell paramagnetism of the $\pi$ electrons is reflected in the characteristic sombrero-shaped curve. For the larger members of the [4$n$]-carbocycles series, the paramagnetic response of the $\pi$ electrons dominates the linear magnetic response. In fact, exactly as for the small closed-shell paramagnetic molecules considered in the previous section, the energy curves for the larger [4$n$]-annulenes $C_8H_8$ and $C_{12}H_{12}$ display the typical sombrero shape, characterizing the paramagnetic-to-diamagnetic transition of their RHF closed-shell ground state as a function of the external field strength; however, for these larger molecules, the critical field is about one order of magnitude smaller than for the previous systems. We find $B_c \approx 0.032$ a.u. for COT, and $B_c \approx 0.016$ a.u. for the [12]-annulene.

Clearly, the magnitude of the critical field $B_c$ decreases with system size. In particular, since orbital magnetism is proportional to the external magnetic flux, we can expect $B_c$ to vary roughly as the inverse of the area of the molecule. Therefore, since the area of a regular $N$-sided polygon with sides of length $l$ is given by

$$A_N = \frac{Nl^2}{4\cot\left(\frac{\pi}{N}\right)} \approx \frac{N^2l^2}{4\pi},$$

it follows that, if we take a ring six times larger than $C_{12}H_{12}$, the energy minimum should be observed for a critical field of about 100 T, which is within reach of current experimental techniques. Therefore, according to this back-of-the-envelope estimate, the ratio between the critical fields of $C_{12}H_{12}$ and $C_8H_8$ is given by $B_{c,12}/B_{c,8} \approx A_{8}/A_{12} \approx 0.43$, comparable with our best basis-set ab initio results $B_{c,12}/B_{c,8} = 0.5$. For these systems, the corresponding singlet–triplet level-crossing field is
estimated to be $B_{LC} \approx 0.02$ a.u. for COT ($\Delta W_T = 0.0179$ a.u.) and $B_{LC} \approx 0.07$ a.u. for C$_{12}$H$_2$ ($\Delta W_T = 0.1395$ a.u.), so that the diamagnetic transition will only occur for the ground state of the latter.

C Antiaromatic closed-shell polycycles: acepleiadylene and corannulene dianions

We finally consider the non-perturbative magnetic response of the acepleiadylene and corannulene dianions. Both systems have been identified as closed-shell paramagnetic molecules by means of ab initio calculations.\textsuperscript{33,34} The bowl-shaped structure for the corannulene dianion was taken from ref. 34. The results of the RHF calculations of the energy as a function of applied perpendicular field are plotted in Fig. 4, where we recognize the features characterising the paramagnetic–diamagnetic transition observed for the smaller systems. The magnitude of the transition field does not vary much with the quality of the basis set. It is of the same order of magnitude as for the antiaromatic rings considered in the previous section, which is not surprising considering the similar spatial extent of these systems. We find $B_c = 0.023$ a.u. (about 5400 T) for the acepleiadylene dianion, similar to the COT value. Note that, as reported in ref. 33, the paramagnetic ring current is mostly localised on the seven membered ring, which is of about the same size as COT. For the corannulene dianion, we find $B_c = 0.015$ a.u. (about 3500 T).

The results for these polycyclic molecules appear to be particularly interesting for engineering larger closed-shell paramagnetic systems. It is well known that the introduction of odd-member ring defects—in particular, pentagonal rings—in a carbon honeycomb lattice leads to an increase of its antiaromaticity,\textsuperscript{37} which, by the magnetic criterion, corresponds to an increase of its paratropicity.\textsuperscript{37–39} Hence, graphene flakes doped with acepleiadylene or corannulene dianion moieties might be expected to give rise to extended closed-shell paramagnetic structures, in which the paramagnetic–diamagnetic transition occurs for relatively small critical fields.

The singlet–triplet level-crossing field for these polycyclic systems is estimated to be $B_{LC} \approx 0.043$ a.u. for C$_{16}$H$_{10}^{2-}$ ($\Delta W_T = 0.5187$ a.u.) and $B_{LC} \approx 0.035$ a.u. for C$_{20}$H$_{10}^{2-}$ ($\Delta W_T = 0.05158$ a.u.). For both systems, therefore, the diamagnetic transition is expected to occur in the ground state.

III. An analytical model for the diamagnetic transition

Why should we expect paramagnetic closed-shell species to become diamagnetic in strong magnetic fields? To answer this question, we consider a very simple model. Two distinguishing features common to all closed-shell paramagnetic systems consist of (i) a totally symmetric ground state (ii) the existence of a low-lying excited state that has the symmetry of a magnetic dipole operator (i.e., of a rotation about the external field). All molecules considered here trivially fulfill the first requirement and can also be shown to fulfill the second requirement. We approximate here the lowest-lying states of the molecular energy spectrum in terms of excitations among frontier molecular orbitals (MOs), so that the lowest-lying excited state corresponds to an excitation between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO).

For instance, six-electron diatomic hydrides such as BH and CH$^+$ can be described in terms of a non-degenerate HOMO, consisting of the sp hybrid (the lone pair) centered about the heavier atom and pointing along the bond axis (say, the $z$ axis), and of a doubly degenerate LUMO, given by the perpendicular $p$ orbitals centered on the heavier atom ($p_x$ and $p_y$ on carbon and boron). If we consider a magnetic field perpendicular to the bond (e.g., along the $y$ direction), the molecular Hamiltonian can be written as

$$H = H_{el} + H_B$$

(3.4)

where $H_{el}$ is the electrostatic Hamiltonian and $H_B$ represents the magnetic interaction (in atomic units):

$$H_B = BL_a - \frac{1}{2} a B^2,$$

(3.5)

where $a$ is the direction of the magnetic field (here $y$) of strength $B$. The magnetic Hamiltonian contains two contributions: first, the orbital Zeeman term $BL_a$, where $L_a = \sum_{i} l_{a,i}$ is
the component of the angular-momentum operator in the direction of the field (centered on the heavy atom); second, a diamagnetic term $-\chi_d^g B^2$, where $\chi_d^g$ is one half of the diamagnetic susceptibility operator—for example, $\chi_d^g = -\sum (\lambda_i^g + \lambda_i^g)^2/8$.

Thus, denoting the HOMO by $\psi_{\mathrm{H}}$ and the LUMO by $\psi_{\mathrm{L}}$, we find that the Hamiltonian matrix elements between the ground state $\Psi_0 = |\phi_{\mathrm{H}}\phi_{\mathrm{L}}\phi_{\mathrm{H}}\phi_{\mathrm{L}}\rangle$ and the doubly degenerate first excited states 

$\Psi_{1x} = 2^{-1/2} |\phi_{\mathrm{H}}\phi_{\mathrm{L}}\phi_{\mathrm{L}}\phi_{\mathrm{L}}\rangle + \phi_{\mathrm{L}}\phi_{\mathrm{H}}\rangle$ and $\Psi_{1y} = 2^{-1/2} |\phi_{\mathrm{H}}\phi_{\mathrm{L}}\phi_{\mathrm{L}}\phi_{\mathrm{L}}\rangle + \phi_{\mathrm{L}}\phi_{\mathrm{H}}\rangle$ are given by:

$$\langle \Psi_0 | H | \Psi_{1x} \rangle = \sqrt{2} \langle \phi_{\mathrm{H}} | l_x | \phi_{\mathrm{L}} \rangle B,$$  

(3.6)

$$\langle \Psi_0 | H | \Psi_{1y} \rangle = \sqrt{2} \langle \phi_{\mathrm{H}} | l_y | \phi_{\mathrm{L}} \rangle B,$$  

(3.7)

since the matrix elements of $H$ and of the diamagnetic part of $H$, eqn (3.5), between the ground and degenerate excited states are zero by symmetry. On the other hand, the transition is clearly rotationally allowed.

The HOMO is a combination of the hybrid sp$_{z,x}$ on the heavy atom (where $x$ is B or C) and 1s$_{\mathrm{H}}$ on hydrogen:

$$| \phi_{\mathrm{H}} \rangle = \lambda (a | 1s_{\mathrm{H}} \rangle + b | 2s_{\mathrm{H}} \rangle + c | 2p_{z,x} \rangle)$$  

(3.8)

$$\lambda = (a^2 + b^2 + c^2 + 2ah S_{1s_{\mathrm{H}} 2s_{\mathrm{H}}} + 2ac S_{1s_{\mathrm{H}} 2p_{z,x}})^{-1/2}$$  

(3.9)

where $S_{1s_{\mathrm{H}} 2s_{\mathrm{H}}}$ and $S_{1s_{\mathrm{H}} 2p_{z,x}}$ are the relevant overlap integrals. If we choose the quantization axis for $L$ along the $y$ axis, it is possible to write the irreducible tensor representation of the operators and orbitals appearing in the matrix elements eqn (3.6) and (3.7) as $l_x \equiv l_0$, $2p_y \equiv p_0$, $2p_z \equiv 2^{-1/2}(p_1 + p_{-1})$ and $2p_{x,y} \equiv 2^{-1/2}(p_1 - p_{-1})$. An estimate of the Hamiltonian matrix elements between the ground state and the first excited singlet states eqns (3.6) and (3.7) can then be easily provided:

$$\langle \Psi_0 | H | \Psi_{1x} \rangle \approx \frac{1}{N} \langle \phi_{\mathrm{H}} | \lambda (p_1 + p_{-1}) | l_0 \rangle B \quad = i \mu B$$  

(3.10)

$$\langle \Psi_0 | H | \Psi_{1y} \rangle \approx \frac{1}{N} \langle \phi_{\mathrm{H}} | \lambda (p_1 - p_{-1}) | l_0 \rangle B = 0$$  

(3.11)

with $\mu = \lambda c$.

Similar arguments can be made for the other closed-shell paramagnetic systems considered here, to identify those states that contribute strongly to the mixing in a strong magnetic field. For instance, from the theory of ring currents in planar conjugated $\pi$ systems, it is known that the paramagnetic ring currents in [4n]-annulenes stem from the rotationally allowed HOMO–LUMO transition.

Considering a fully symmetric $D_{Nh}$ [$N$]-carbocycle in a minimal basis of one $p_{z,x}$ atomic orbital per carbon center, we can write the $N$ symmetry adapted $\pi$ MOs as:

$$| \psi_x \rangle = N^2 \sum_s \exp \left( i \frac{2\pi \lambda x N}{r} \right) | p_{z,x} \rangle$$  

(3.12)

$$N^2 \cos \left( \frac{2\pi \lambda x N}{r} \right) \left( N + 2 \sum_{r>s} S_{rs} \cos \left( \frac{2\pi \lambda x N}{r - s} \right) \right)^{-1/2},$$  

(3.13)

where, for even $N$, $\lambda = 0, \pm 1, \pm 2, \ldots, \pm N/2$, and the overlap integrals are given by $S_{rs} = \langle p_{z,x} | p_{z,x} \rangle$. It follows that $\lambda$ is a good rotational quantum number, so that for the one-particle states we can write:

$$l_x | \psi_x \rangle = \lambda | \psi_x \rangle$$  

(3.14)

From these simple symmetry-based considerations, it follows that all [4$n$]-carbocycles of full $D_{Nh}$ rotational symmetry have an orbitally degenerate ground state, since the HOMO and LUMO are rotational pairs with $\lambda = \pm n$, belonging to a doubly degenerate irreducible representation. According to the Jahn–Teller theorem, vibronic coupling removes this degeneracy by reducing the symmetry to at least $D_{2n}$, corresponding to the structures considered here: $C_8H_4$ of $D_8h$ symmetry, $C_{4n}H_{4n}$ of $D_{2n}$ symmetry, and $C_{12}H_{12}$ of $D_{6h}$ symmetry. This symmetry reduction leads to new one-particle states, resulting from a well-defined mixing pattern between the states of the fully symmetric parent so that each occupied angular momentum shell eqn (3.12) with $\lambda \leq n$ is solely mixed with a virtual shell having $\lambda = N/2 - \lambda$. Thus, in closed-shell [4$n$]-annulenes, the HOMO ($\psi_H$) and LUMO ($\psi_L$) are non-degenerate, resulting from a mixing between the doubly degenerate HOMO and LUMO of the fully symmetric open-shell parent:

$$\psi_H = \frac{1}{\sqrt{2}} (| \psi_a \rangle + | \psi_{-a} \rangle),$$  

(3.15)

$$\psi_L = -i \frac{1}{\sqrt{2}} (| \psi_a \rangle - | \psi_{-a} \rangle).$$  

(3.16)

Omitting from the notation all closed-shell orbitals that do not contribute to the coupling, we may write the ground and first excited states as $\Psi_0 = | \psi_{\mathrm{H}} \psi_{\mathrm{L}} \rangle$ and $\Psi_1 = | 2^{-1/2} \psi_{\mathrm{H}} | \psi_{\mathrm{L}} \rangle + | \psi_{\mathrm{H}} \psi_{\mathrm{L}} \rangle$, respectively. The coupling by the magnetic Hamiltonian in eqn (3.5) (with $a = z$) can then be written as:

$$\langle \Psi_0 | H | \Psi_1 \rangle = \langle \psi_{\mathrm{H}} | l_z \psi_{\mathrm{L}} \rangle B = i B 0 \equiv i \mu B$$  

(3.17)

We can thus proceed to write a very general effective coupling Hamiltonian, valid for all closed-shell paramagnetic molecules in strong magnetic fields as:

$$H = \begin{pmatrix} -\Delta + \chi_d B^2 & i \mu B \\ -i \mu B & -\Delta - \chi_d B^2 \end{pmatrix},$$  

(3.18)

where $2\Delta$ is the energy gap between the two states in zero-field, and $\chi_{d,0} \equiv \langle \Psi_{0,0,0} \rangle = \langle \Psi_{0,0,0,0} \rangle < 0$. Without loss of generality, we assume in the following that $\mu > 0$. The ground- and excited-state energies as functions of the external field strength, $B$, are straightforwardly obtained by diagonalising eqn (3.18), giving

$$W_{0/1}(B) = -\frac{1}{2} (\chi_0 + \chi_1) B^2 + \frac{1}{2} \sqrt{2 \Delta^2 + (\chi_0 - \chi_1) B^2 + 4 \mu^2 B^2},$$  

(3.19)

where the minus sign is used in the ground-state energy $W_0(B)$ and the plus sign in the excited-state energy $W_1(B)$.

Let us now investigate how the energies of the ground and excited states depend on the magnetic field, $B$, which may take on negative as well as positive values. We first consider briefly
the case of no interaction between the two states, \( \mu = 0 \). The energies eqn (3.19) may then be written as:

\[
W_{0/1}^0(B) = \mp \Delta - Z_0/B^2, 
\]

which become degenerate and cross each other at \( B = \sqrt{2\Delta/(Z_0 - Z_1)} \) if \( |Z_0| > |Z_1| \). As expected, both states are diamagnetic in this case, with a minimum at \( B = 0 \). This situation is illustrated in Fig. 5a, for a system with (atomic units) \( \Delta = 0.01, Z_0 = -7.0, \) and \( Z_1 = -4.0 \).

When \( \mu \neq 0 \) and the two states avoid each other and no crossing may occur: the ground state is paramagnetic for \( \mu^2 > |Z_0| \), see (d), the ground state energy is described by the sombrero shape observed in ab initio calculations.

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W_{0/1}^{\mu}(B) = \mp \Delta - Z_0/\mu^2, 
\]

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which become degenerate and cross each other at \( B = \sqrt{2\Delta/(Z_0 - Z_1)} \) if \( |Z_0| > |Z_1| \). As expected, both states are diamagnetic in this case, with a minimum at \( B = 0 \). This situation is illustrated in Fig. 5a, for a system with (atomic units) \( \Delta = 0.01, Z_0 = -7.0, \) and \( Z_1 = -4.0 \).

When \( \mu \neq 0 \) and the two states avoid each other and no crossing may occur: the ground state is paramagnetic for \( \mu^2 > |Z_0| \), see (d), the ground state energy is described by the sombrero shape observed in ab initio calculations.

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appearance of the sombrero-shaped ground-state energy curve when \( \mu^2/2 \Delta > |\langle \psi_0 \rangle| \), that is, when the system becomes closed-shell paramagnetic. Interestingly, for \( \mu^2/2 \Delta \approx |\langle \psi_0 \rangle| \) in Fig. 5c, we obtain a diagram that is very similar to the cyclobutadiene \textit{ab initio} energy plot in Fig. 2a. Using eqn (3.19) to fit the cc-pVDZ total energy curve of butadiene.

Fig. 6 On the left column, the energy curves obtained by fitting the best \textit{ab initio} ground state energy data points (reported as black dots) for (a) BH, (c) CH\(^+\), (e) C\(_{16}\)H\(_{10}\)^{2\text{−}} and (g) C\(_{20}\)H\(_{10}\)^{2\text{−}} with eqn (3.19) (solid line) are compared to the energy curves obtained by fitting the same data with a sixth-order polynomial (dotted line) and an eighth-order polynomial (dashed line). On the right column, the critical field \( B_c \) is plotted as a function of the effective gap \( 2 \Delta |\langle \psi_0 \rangle|/\mu^2 \) for (b) BH, (d) CH\(^+\), (f) C\(_{16}\)H\(_{10}\)^{2\text{−}} and (h) C\(_{20}\)H\(_{10}\)^{2\text{−}} using eqn (3.23) with the gap \( \Delta \) varying between zero and \( \Delta_{\text{max}} = \mu^2/2 |\langle \psi_0 \rangle| \), and the other three parameters fixed to their best \textit{ab initio} values. The plots can be understood as “phase diagrams”, in that they define regions of existence of paramagnetic and diamagnetic “phases” in parameter space. The superimposed gridlines identify the exact values of the reduced gap and of \( B_c \) characterizing the \textit{ab initio} energy minimum.
we obtain $\mu^2/2A \approx 4.8$ a.u. and $|\chi_0| \approx 5.2$ a.u., so that $\mu^2/2A \approx |\chi_0|$, confirming that, due to its strong π-electron paratropicity, the onset of global paramagnetism is indeed quite close in cyclobutadiene.

The two-level model also proves very useful for obtaining an approximate analytical fit to the ab initio data, accurate for a large range of field strengths. In Fig. 6 (left column), for instance, we report the energy versus field ab initio data points, together with a least-squares fit to the data of a sixth-order polynomial (dotted line), of an eighth-order polynomial (dashed line), and of the ground-state energy of the two-state model eqn (3.19) (solid line). The two-state model invariably produces an accurate fit to the data, whereas the sixth- and eighth-order polynomial fits based on the Taylor perturbative expansion eqn (1.1) perform poorly, especially for the smaller systems, where larger ranges of magnetic field strengths are considered.

One quantitative measure of the quality of the fitted energy functions provided by eqns (1.1) and (3.19) can be obtained by comparing the relevant diagonal component of the linear magnetizability tensor computed by taking the first derivative at zero field of the fitted expressions, with the exact value calculated by means of response theory. To produce the most accurate estimate for linear response by finite-field methods in a highly non-linear system, it is clearly expedient to consider a set of data points corresponding to very small fields in the optimization procedure. We consider here only four systems—namely, BH, CH⁺, the aceplaidylene dianion, and the corannulene dianion—taking only the first four values for each set of data points corresponding to the plots in Fig. 2 and 4. The results are reported in Table 1. Bearing in mind that the range and number of points were not optimised for accuracy, it is clear from Table 1 that the expression in eqn (3.19) invariably delivers more accurate zero-field second derivatives than does eqn (1.1). In addition, the two-state model provides a better description of the energy variation in the high-field regime.

A suggestive explanation for the difficulties of finding accurate polynomial representations of the energy curve is provided by our model energy curve. The Taylor series of the function $\sqrt{1 + x}$, expanded around $x = 0$, has the radius of convergence $|x| < 1$. From this it follows that a Taylor expansion of our model energy has a radius of convergence given by:

$$B_{\text{conv}}^2 = \frac{2}{\delta_x^2} \left( (4\delta_x + \mu^2)^2 + 4\delta_x^2 - 4\delta_x - \mu^2 \right).$$

### Table 1

Linear magnetizability (positive diagonal component) for BH, CH⁺, C₆H₆⁻ and C₈H₄⁻ calculated as (i) a linear response function ($\chi_{\text{L, response}}$), (ii) a second derivative of the ab initio fitted two-level model energy ($\chi_{\text{L, model}}$), and (iii) a second derivative of the ab initio fitted eighth-order polynomial ($\chi_{\text{L, poly8}}$), using an (aug)-cc-pVDZ basis of London orbitals.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\chi_{\text{L, response}}$</th>
<th>$\chi_{\text{L, model}}$</th>
<th>$\chi_{\text{L, poly8}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH</td>
<td>7.154</td>
<td>7.151</td>
<td>7.100</td>
</tr>
<tr>
<td>CH⁺</td>
<td>10.330</td>
<td>10.315</td>
<td>10.218</td>
</tr>
<tr>
<td>C₆H₆⁻</td>
<td>38.398</td>
<td>38.394</td>
<td>38.342</td>
</tr>
<tr>
<td>C₈H₄⁻</td>
<td>70.419</td>
<td>70.419</td>
<td>70.253</td>
</tr>
</tbody>
</table>

Finally, it is interesting to note that the critical field eqn (3.23) plotted as a function of the reduced gap $2\Delta(\chi_0)/\mu^2$ can be understood as an effective “phase diagram”, which separates the diamagnetic and paramagnetic “phases” as functions of the applied field and the effective gap. In Fig. 6 (second column), we have plotted these diagrams, where the gap varies between zero and $\Delta_{\text{max}} = \mu^2/2|\chi_0|$, while the remaining three parameters are set to their optimal cc-pVDZ values (aug-cc-pVDZ for BH and CH⁺). The superimposed grid lines correspond to the exact values of the reduced gap and of the critical field characterizing the energy minimum associated with the real system.

Furthermore, we note that the reduced gap is the ratio between the diamagnetic and paramagnetic components of the two-state-model linear magnetizability, so that both magnetic phases can exist only if the effective gap is smaller than one. Accordingly, these plots show that the closer the effective gap value is to one—that is, the less paramagnetic the system is—the smaller is the critical field at which the molecule turns diamagnetic. Thus, if it were possible to modulate the effective energy gap (i.e., to decrease the value of the positive linear magnetizability) by means of some additional perturbation (electric fields, substituent effects, etc.), it would be possible to tune the value of the transition field.

### IV. Conclusions

We have investigated the non-linear magnetic behaviour of a set of organic and inorganic paramagnetic closed-shell molecules in strong magnetic fields. We found that all the systems considered are characterized by a similar behaviour in strong fields, in that the paramagnetic system turns diamagnetic when the field is larger than a critical value $B_c$. Moreover, a simple two-level model was developed to rationalize this phenomenon. The model provides both a useful energy expression to fit ab initio data and a demonstration that such behaviour should be expected for any paramagnetic closed-shell molecule. Because of their small size, the systems considered here require magnetic fields at least one order of magnitude larger than what can be achieved experimentally to undergo the diamagnetic transition. However, the same transition should occur for experimentally attainable fields if larger systems (containing about 100 atoms) are considered, due to the enhancement of the effective magnetic flux. Interestingly, a straightforward analysis of the simple model hereby proposed suggests that it might be possible to tune the transition field by means of external perturbations capable of modulating the paramagnetic linear response of the closed-shell molecule.
References


