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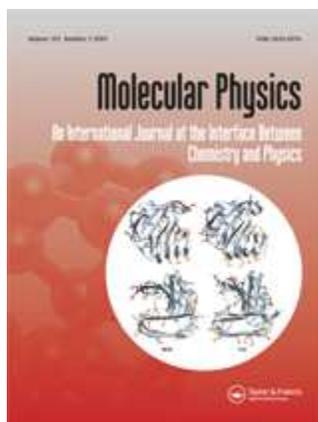
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Aromaticity of planar Si₆ rings in silicon-lithium clusters

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Abstract

Ipsocentric calculations of current density at the B3LYP/6-311++G(2d,2p) level show that the planar Si₆ ring supports a diatropic π ring current of about half the strength of the equivalent π current in benzene, both in the presumed global optimum geometry of Si₆Li₆ and in geometries occupying higher-energy local minima, corroborating the attribution of aromaticity to this silicon analogue of benzene.

Introduction

Aromaticity is a term that is typically applied to planar π -bonded carbocycles, and one that may appear to have little relevance to silicon chemistry, where three-dimensional σ -bonded polyhedral clusters predominate [1]. Certainly, direct analogies with carbon structures can often be misleading. For example, Si₆H₆ does not have the planar D_{6h} structure that comparison with C₆H₆ would suggest [2]. A π -bonded planar Si₆ ring has been predicted, but as a component of a neutral D_{2h}-symmetric Si₆Li₆ cluster, indicated by extensive computational search as the equilibrium structure for that stoichiometry [3,4], and giving new point to exploration of the carbon-silicon aromaticity analogy.

A proposed rule of thumb [3,4] suggests that replacement of carbon by valence isoelectronic silicon, accompanied by replacement of hydrogen with valence isoelectronic lithium (in an appropriate geometry) should lead to an aromatic species. How might such a statement be tested? What criterion should be used? Aromaticity is traditionally assessed according to various criteria, typically based on energetics, reactivity, geometry or magnetic response [5]. The advantage of the magnetic criterion is its absolute character: if a cyclic system supports a diatropic, paratropic or

vanishing ring current, it is classified as aromatic, anti-aromatic or non-aromatic, respectively. No further reference is needed.

In the present note, we apply this criterion to isomers of Si_6Li_6 and related species in a direct manner, by computing the current density induced in the silicon ring by a perpendicular magnetic field, mapping it and checking the map for global circulation. Comparison with alternative low-energy structures shows that the D_{2h} Si_6Li_6 cluster is in key respects a π -aromatic, in spite of the three-dimensional coordination of the Si_6 ring. Scheme 1 shows the structures studied here, which comprise three isomers [3,6] of Si_6Li_6 , a proposed [6] $\text{Si}_6\text{Li}_8^{2+}$ cation incorporating the same planar Si_6 ring, and the planar form of the carbon analogue C_6Li_6 .

Scheme near here

Geometries for **1-3** and **5**, obtained at the B3LYP/6-311++G(2d,2p) level, were taken from [3], and that for **4** was optimised at the same level of theory using the GAMESS-UK program [7]. The optimised bond-lengths (in Å) for all five structures are shown in the Scheme. Calculations of the induced current density within the ipsocentric approach to molecular magnetic response were performed at the CHF [8-10] and DFT [11] levels of theory using the SYSMO package [12], and maps were constructed for the total, canonical [10] and localised [13] RHF/Kohn-Sham orbital contributions to current. (Localised orbitals were obtained with the Pipek-Mezey procedure [14]). For carbocyclic systems, maps of π ring current are generally plotted at a height of $1a_0$ from the molecular plane; here, current was probed at several heights from the Si_6 plane to establish the appropriate height for second-row atoms (it turns out that the maximum in π -current density is at $\sim 1.5 a_0$ for Si rings) and, in the case of the non-planar species (**1**, **3**), to check separability of π and out-of-plane lithium contributions. Maps for σ current density were plotted at a height of $0.3 a_0$, to strike a balance between maximisation of response, which occurs in the molecular plane, and the need to avoid the visual confusion caused by highly localised core currents. Maps were constructed at both CHF and DFT levels of theory, but showed only small differences; only the DFT maps are shown here, as representative of both. An indication of the strength of ring current, and of the small differences between CHF and DFT results, is the maximum value of the current per unit inducing field, j_{\max} , which gives a useful comparison with the typical aromatic, benzene; j_{\max} calculated at the RHF/6-31G** level for the π current in benzene at a height of $1 a_0$ is 0.08 a.u. [15]. Other standard plotting conventions apply: arrows show the in-plane projection, and contours the magnitude, of the current-density induced per unit external field; anti-clockwise circulations in the maps indicate diatropic (diamagnetic) current.

Results

(i) Height profiles

Tests to establish the best height at which to plot π current density for the Si_6 ring are summarised in Figure 1, which shows an analysis of π current density for species **1-3** as a function of height from the silicon plane. As might be expected for a π current density arising from 3p atomic orbitals, the π circulation in these species is zero in the central plane, grows to a maximum in the region of 1-2 a_0 and then falls to zero. The maximum in the profile occurs close to 1.5 a_0 , and this is taken in what follows to be the standard height for the π current-density maps of the Si_6 -containing species.

Figure 1 near here

(ii) Aromaticity of Si_6Li_6 in the low-energy D_{2h} structure

Figure 2 shows computed current-density maps for the D_{2h} structure **1**. Although the molecule is not planar, π -like orbitals can be identified by their symmetry with respect to the median plane. The nodal characteristics of the $4b_{1u}$, $3b_{2g}$ and $2b_{3g}$ valence orbitals establish them as ' π ' with respect to the Si_6 plane, and their summed contribution is plotted, as the map of total π current density at a height of 1.5 a_0 (Fig. 2a). At the B3LYP/6-311++G(2d,2p) level, the three 3p-derived π orbitals are HOMO-2, HOMO-4 and HOMO-6, respectively; at the RHF level they are HOMO-1, HOMO-3 and HOMO-6. The separate contributions of the highest-lying b_{3g} and b_{2g} orbitals (Figs 2b, 2c) dominate the π map, and the sum of their contributions is visually indistinguishable from the total π map. There is a clear global π ring current in this molecule, arising from the four electrons of the top two π orbitals, and this is a diatropic current, indicating aromaticity according to the magnetic criterion.

Figure 2 near here

The qualitative explanation of π ring currents in the ipso-centric approach is based on node counting [16]. Each perturbed occupied orbital contains admixtures of unoccupied orbitals which can be interpreted in terms of sums over virtual excitations: a 'translational' excitation from an occupied orbital is allowed if initial π and final π^* orbitals differ by one angular node and then generates a diatropic contribution; a 'rotational' excitation is allowed if initial π and final π^* orbitals have the same number of angular nodes and then generates a paratropic contribution. In D_{6h} symmetry, these angular-momentum based rules have precise symmetry equivalents, and so for

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3 benzene the only allowed excitation within the π valence space is from HOMO to LUMO and the
4 ring current is attributable to the magnetic response of four electrons.
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7 **Figure 3 near here**

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9 In the reduced D_{2h} point group of **1**, the symmetry rules are relaxed (see Fig. 3), but the nodal
10 characters of the frontier canonical orbitals are preserved, so that the ring current remains diatropic
11 and dominated by the four electrons of the (split) π -HOMO. This four-electron current is the
12 magnetic signature of aromaticity [16].
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16 Thus, D_{2h} Si_6Li_6 satisfies the definition of aromaticity, in that it sustains a significant π ring
17 current. In terms of magnitude, however, the magnetic response of the Si_6 ring in **1** is predicted to
18 be about half that of benzene (Fig. 1). This ratio is perhaps not unexpected in view of the poorer π
19 bonding ability of second-row atoms.
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23 The close analogy with the π electronic structure of benzene also emerges from a localised-
24 orbital analysis. For both molecules, Pipek-Mezey localisation of the π occupied orbitals is only
25 partly successful, in that although a set of three more-or-less spatially confined orbitals (in fact, an
26 infinite family of such sets) is produced, their contributions to the induced current density show
27 open flow-lines (Fig. 4). As discussed in [13], this is an indication of the intrinsic delocalisation of
28 the π electrons. A closed circulation (the global ring current) is recovered only on summation of the
29 three contributions. In a localised π system, the current pattern would be most economically
30 expressed in terms of closed loops of current arising from just a few localised orbitals; for a
31 delocalised π system, as here, the canonical picture is more compact and more natural.
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40 **Figures 4 and 5 near here**

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42 In contrast, the σ orbitals are intrinsically localised in both systems (see [13] for the case of
43 benzene) and their current contributions in **1** are closer to typical 'bond-pair' and 'lone-pair' closed
44 circulations. The σ current-density maps for **1** exhibit overall diatropicity (Fig. 5), but as the
45 localised-orbital analysis shows, this arises from a summation of localised currents, and is not an
46 indication of global σ ring current: the Si-Si bonds and Si lone pairs that emerge from the
47 localisation analysis all give rise to closed local circulations, perturbed by interaction with the in-
48 plane lithium atoms. The summed contributions of the Si-Si bonds account for the typical [15]
49 paratropic vortex at the centre of the maps of total current density, and the contributions of the Si
50 lone pairs give a characteristic 'string-of-pearls' pattern around the perimeter.
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(iii) Aromaticity of other isomers of Si₆Li₆?

Two other isomers of Si₆Li₆ containing planar Si₆ rings have been considered in the recent literature (**2** and **3**, Scheme 1) [3,6]. Of these, one (**2**) has D_{6h} symmetry, with all six lithium nuclei in Si-Si bridging positions. This structure has been identified as occupying a minimum on the potential energy hypersurface [3,6] but it lies some 2.07 eV higher than **1** at the B3LYP/6-311++G(2d,2p) level of theory, and lies above several non-planar isomers (see Fig. 2 and Table 1 of [3]). (The structure **1** was apparently not considered in the B3LYP/6-311G(d) study reported in [6].) Isomer **2** has 6 π valence electrons, occupying 2a_{2u} and 2e_{1g} orbitals which appear as HOMO and HOMO-3 at the B3LYP/6-311++G(2d,2p) level of theory. As Fig. 6a shows, **2** exhibits a diatropic π current similar to that of **1** and to the classic ring current of benzene. Orbital analysis using canonical MOs confirms that the ring current has its origins in the lowest π - π^* virtual excitation, as in benzene, and analysis using Pipek-Mezey localised orbitals confirms the intrinsically delocalised nature of the π system, again in strict analogy with benzene. The strength of the π current is similar in isomers **1** and **2**; in both cases, the maximum current is just under half that in benzene itself (Fig. 4).

Interestingly, comparison of NICS [17] values (listed in Table 2 of [3]) would suggest a more marked difference between the two isomers, with **1** having values that would normally be taken as only equivocal evidence of aromaticity (**1**: NICS(0)= -3.95 ppm, NICS(1)= -4.73 ppm) but **2** having values (**2**: NICS(0)= -5.96 ppm, NICS(1)= -7.38 ppm) that lie substantially closer to those of benzene and similar systems. Isotropic NICS values depend on a mixture of σ and π , local and non-local effects, which may disguise pure 'ring-current' contributions. The σ currents in **2** (Fig. 6) as those of **1**, display lithium-perturbed Si-Si bond and lone-pair circulations, and the usual [15] central paratropic vortex.

Figures 6 and 7 near here

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The lithium-bridged isomer **2** has its carbocyclic analogue in **4**, which has been proposed as the structure of the reported hexalithiobenzene molecule [18,19]. It appears that **4** has the lowest energy amongst those candidate structures for this species that include a planar C₆ ring [20-22]. The calculated π current-density map for **4** (Fig. 5b) shows a π ring current of almost the full benzene strength (see also Fig. 2), essentially unaffected by the presence of the lithium atoms. Again, simple comparison of isotropic NICS values (**4**: NICS(0)= -3.22 ppm, NICS(1)= -7.00 ppm; benzene: NICS(0)= -7.60 ppm, NICS(1)= -9.90 ppm [3]) would suggest a greater disparity in current than is evidenced by the maps.

The other proposed isomer of Si₆Li₆ that includes a planar Si₆ ring is D_{3h}-symmetric **3**. This structure occupies a local minimum on the potential energy hypersurface [3,6] 2.72 eV higher than

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1 at the B3LYP/6-311++G(2d,2p) level of theory. With its strong alternation of Si-Si bondlengths ($\Delta R = 0.11 \text{ \AA}$ [3]) and positive NICS values (**3**: NICS(0)= +4.88 ppm, NICS(1)= +1.43 ppm), this isomer has been called anti-aromatic. Inspection of the current-density maps (Fig. 8) suggests a different interpretation. The 6 π valence electrons give rise to a diatropic ring current, weaker than those of **1** and **2** (at about one quarter (CHF) to one third (DFT) of the benzene strength), but nonetheless present. The π system of **3** must therefore be considered as at least weakly aromatic.

Figure 8 near here

It is known that the π ring current of benzenoid systems can survive substantial bond alternation if the topology of the frontier orbitals is maintained [23]; in this respect, **3** can be seen as an analogue of benzene, with saturated 'clamping' groups [24] that enforce bond-length changes without interfering with the nodal character of the frontier orbitals.

The σ map has a more complex structure: the net effect of the contributions of the six Si-Si bonds and the six Si lone pairs found by application of the Pipek-Mezey procedure is to produce a central paratropic vortex, diatropic features associated with the shorter Si-Si bonds and weak paratropic features near the coordinated lithium centres. Apparently this complicated pattern of cancelling and reinforcing local contributions is what leads to the small positive NICS values.

(iv) Aromaticity of the Si₆ motif in Si₆Li₈²⁺

There are indications that it may be possible to incorporate the Si₆ ring in larger assemblies. As part of their quest for aromatic silabenzene, Santos and Fuentealba [6] constructed theoretical models of cationic clusters by double capping of **2** with either Li⁺ or Na⁺ ions and found D_{6h}-symmetric local minima for both. Current-density maps (Fig. 9) for Si₆Li₈²⁺ (**5**) show that the diatropic π ring current of the planar Si₆ ring survives in the larger cluster, with the same strength as in **2**. The σ currents in the two systems are also closely similar. The maps confirm the robustness of the (magnetic) aromaticity of a single Si₆ moiety to perturbations that preserve the frontier electronic structure. However, planarity is lost in lithium-coordinated polycyclic assemblies of Si₆ rings [3].

Figure 9 near here

Conclusions

These calculations have reinforced predictions of the π aromatic nature of the planar Si₆ planar ring by making an application of the magnetic criterion of aromaticity in the most direct way, i.e., by mapping the induced currents. This aromaticity is found to be preserved in isomers whose energies range over several eV, which is both a confirmation of the frontier-orbital origin of ring current [16]

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3 and a reminder that automatic assumption of connections between stability and (magnetic)
4 aromaticity can be risky [25].
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7 Returning to the rule of thumb introduced in [3]: we have seen that replacement of carbon by
8 silicon leads to a reduction in π ring current, as would be expected from considerations of atomic
9 radius and orbital overlap. Comparison of currents in benzene and Si_6H_6 suggests a reduction factor
10 of about four for this step ($j_{max} = 0.022$ a.u for (D_{6h} -constrained) Si_6H_6 [26]). The calculations
11 reported here indicate that the next step, of replacement of H by Li, does not, in itself, disrupt the
12 current, and may even enhance it. Comparisons amongst SiLi species further suggest that current
13 and hence aromaticity is resilient to changes in coordination environment of the basic planar
14 moiety.
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24
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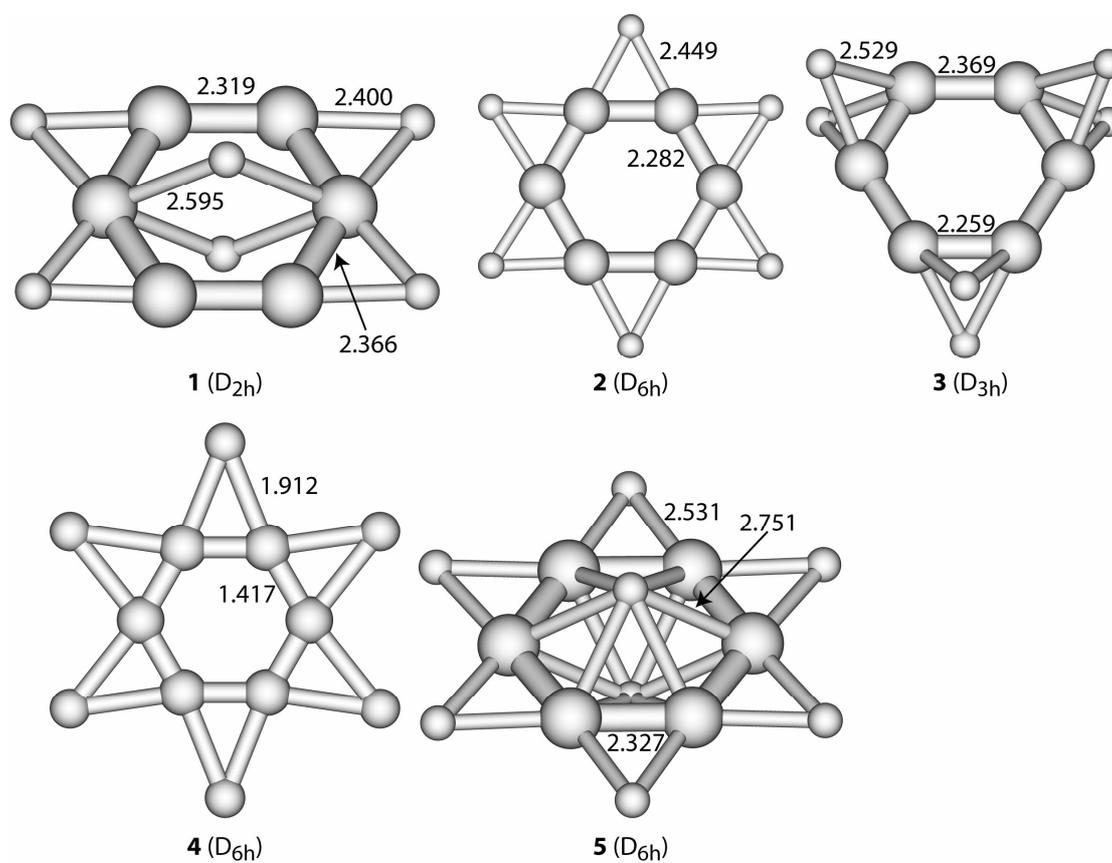
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Legends for Scheme and Figures

- Scheme** The systems under study., showing B3LYP/6-311++G(2d,2p) optimised bondlengths (in Å)
- Figure 1** Variation in the strength of the π current (j in au) of **1-4** (and benzene) as a function of the height (d in a_0). The height is measured from the midpoint of the indicated bond. j is the current density per unit inducing field, expressed in a.u.
- Figure 2** Maps for **1** of a) the π -current density, b) the contribution of the $2b_{3g}$ π -orbital, and c) the contribution of the $3b_{2g}$ π -orbital, all plotted at a height of $1.5 a_0$ from the plane of the Si_6 ring. Plotting conventions are as described in the text; in particular, anticlockwise circulations indicate diatropic currents, clockwise circulations paratropic.
- Figure 3** Orbital energy level diagram for **1**.
- Figure 4** Maps of the contributions of the Pipek-Mezey localised π -orbitals of **1**, plotted at a height of $1.5 a_0$ from the plane of the Si_6 ring. Plotting conventions as in Fig. 2.
- Figure 5** Maps for **1** of a) the σ -current density, b) the sum of the contributions of the localised Si-Si σ -bonds, and c) the sum of the contributions of the localised Si σ -lone-pairs, plotted at heights of $0.3 a_0$ (σ) $1.5 a_0$ (π) from the plane of the Si_6 ring. Plotting conventions as in Fig. 2.
- Figure 6** Maps for **2** of a) the π -current density, b) the σ -current density, c) the sum of the contributions of the localised Si-Si σ -bonds, and d) the sum of the contributions of the localised Si σ -lone-pairs, plotted at heights of $0.3 a_0$ (σ) $1.5 a_0$ (π) from the plane of the Si_6 ring. Plotting conventions as in Fig. 2.
- Figure 7** Maps of a) the π -current density of **4**, and b) the π -current density of benzene, plotted at a height of $1.5 a_0$ from the plane of the C_6 ring. Plotting conventions as in Fig. 2.
- Figure 8** Maps for **3** of a) the π -current density, b) the σ -current density, c) the sum of the contributions of the localised Si-Si σ -bonds, and d) the sum of the contributions of the localised Si σ -lone-pairs, plotted at heights of $0.3 a_0$ (σ) $1.5 a_0$ (π) from the plane of the Si_6 ring. Plotting conventions as in Fig. 2.
- Figure 9** Maps for **5** of a) the π -current density, and b) the σ -current density, plotted at heights of $0.3 a_0$ (σ) $1.5 a_0$ (π) from the plane of the Si_6 ring. Plotting conventions as in Fig. 2.

Scheme



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Figure 1

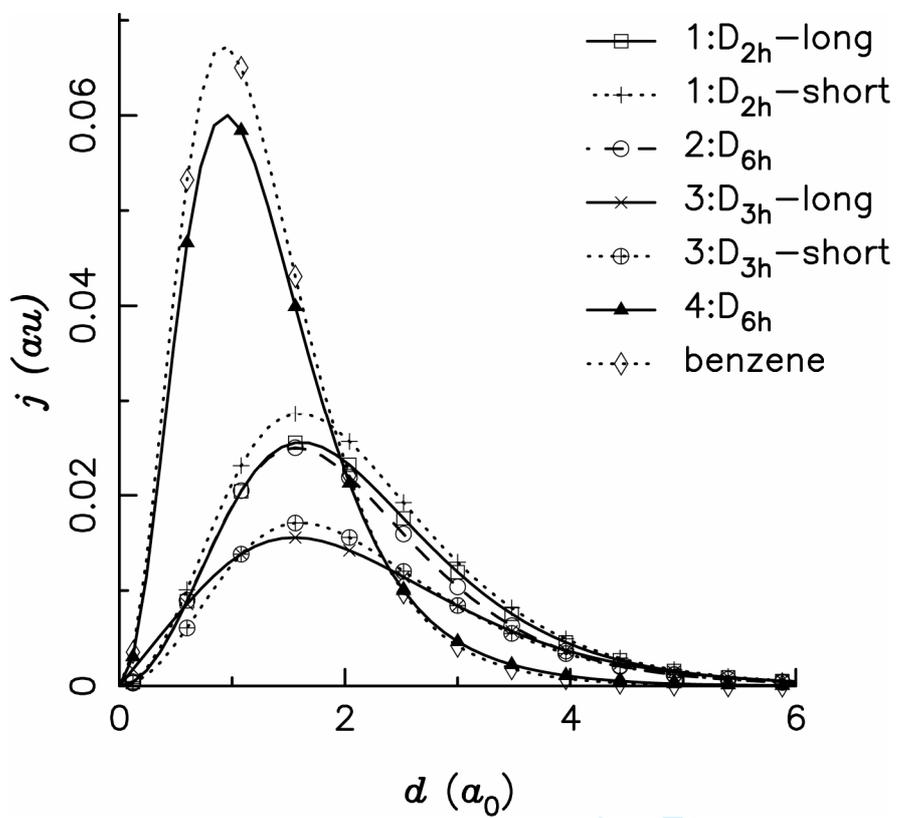


Figure 2

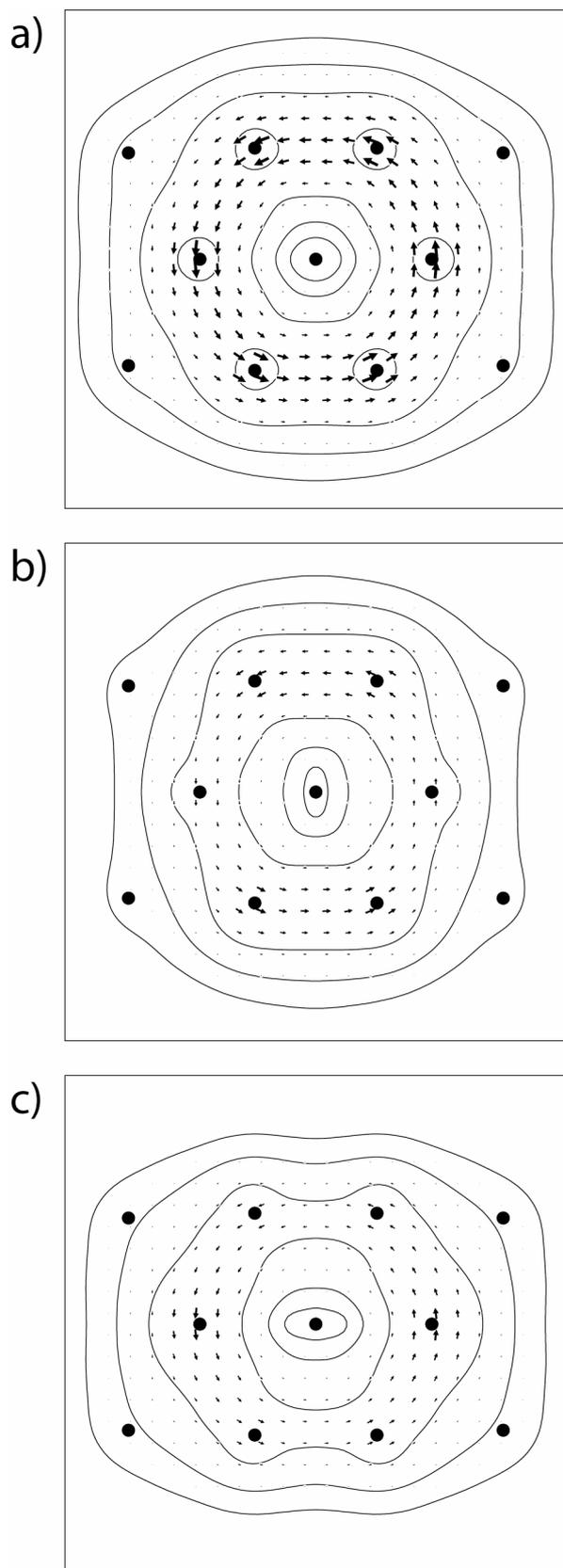


Figure 3

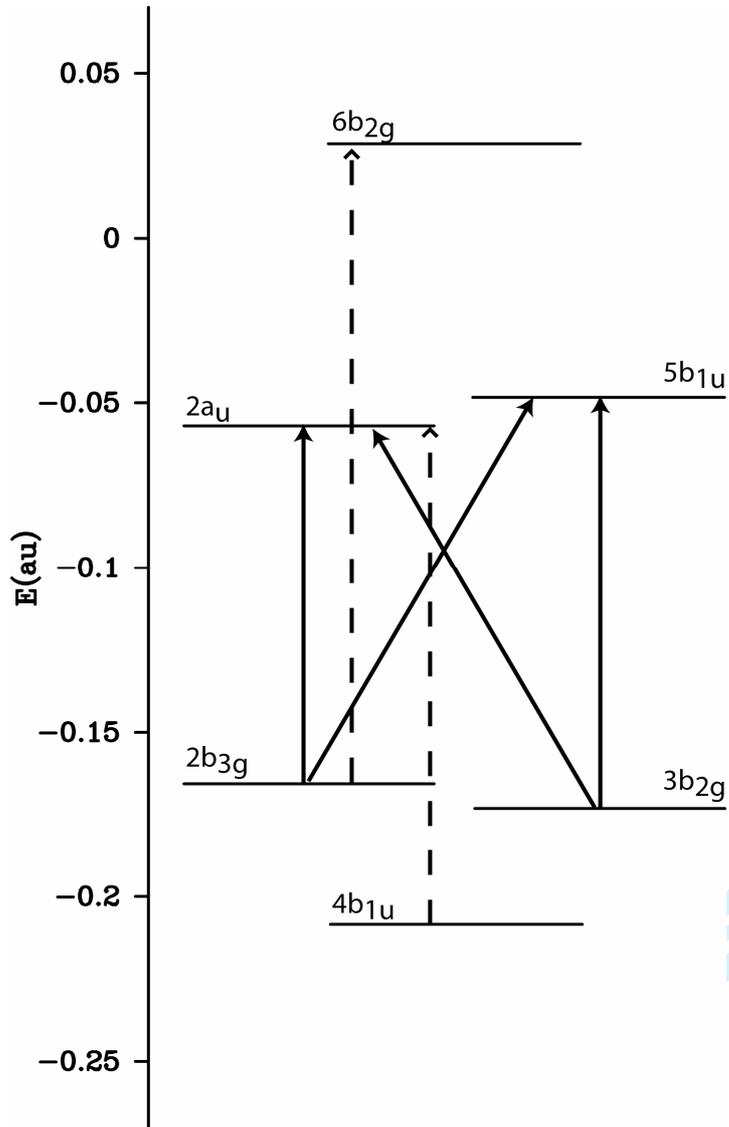


Figure 4

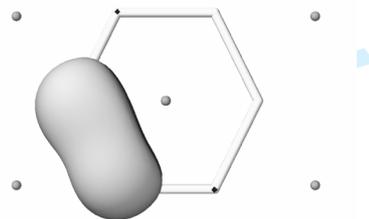
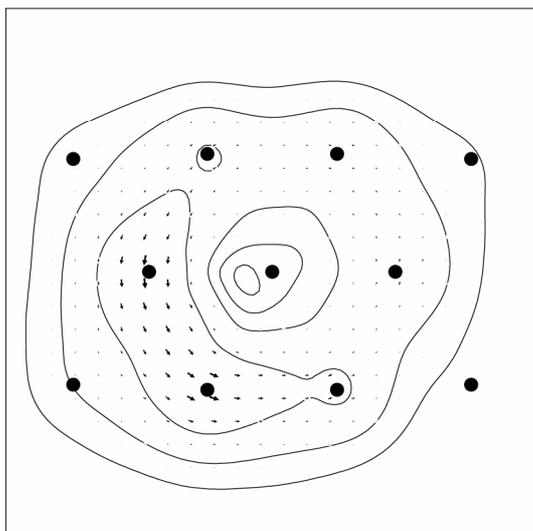
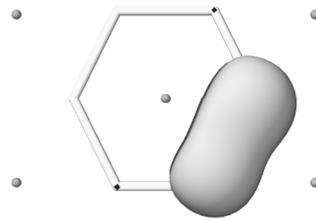
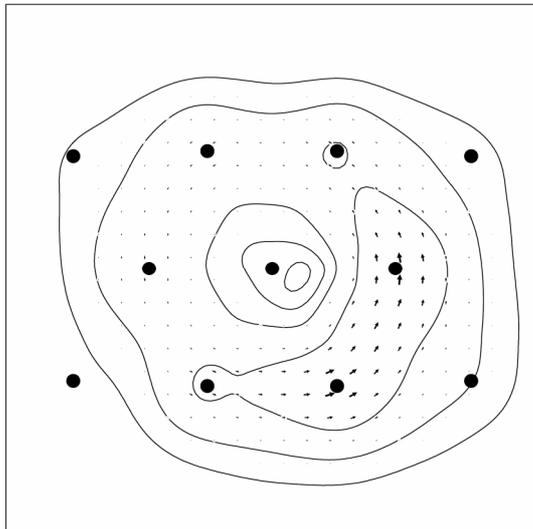
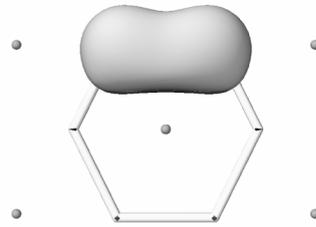
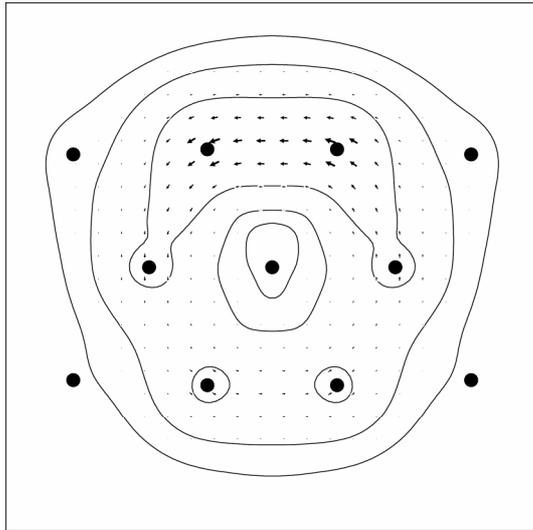
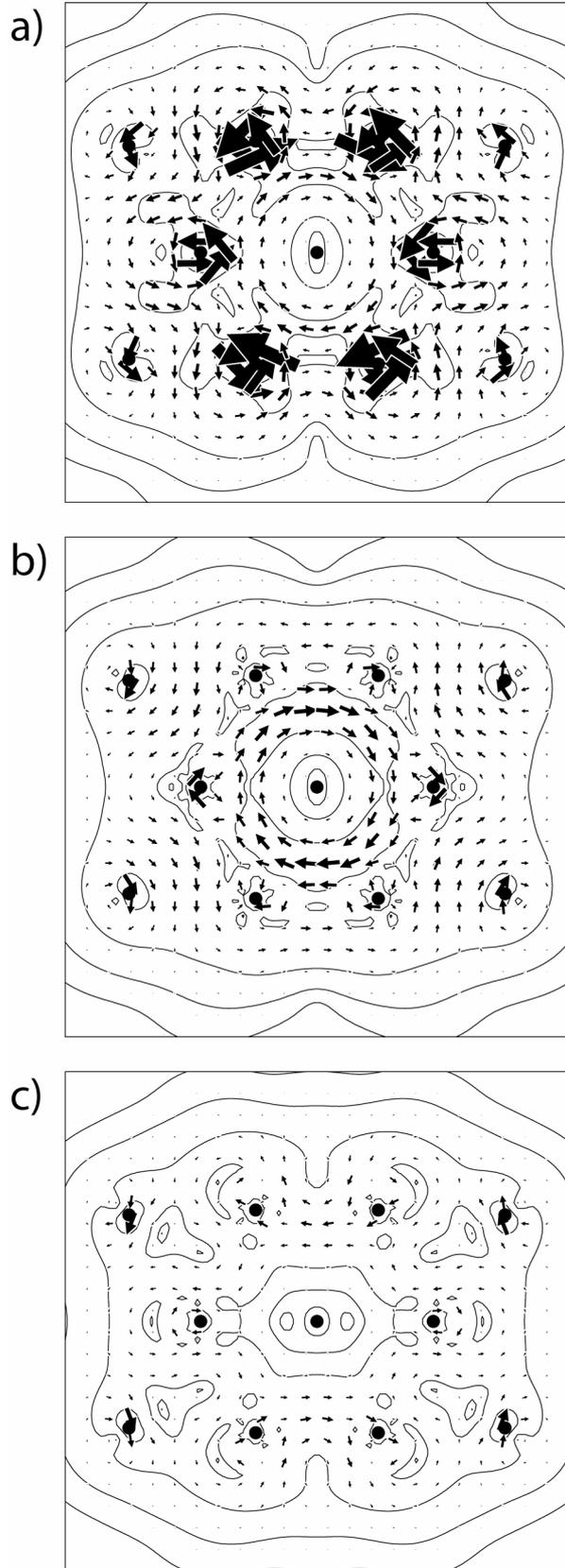


Figure 5



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Figure 6

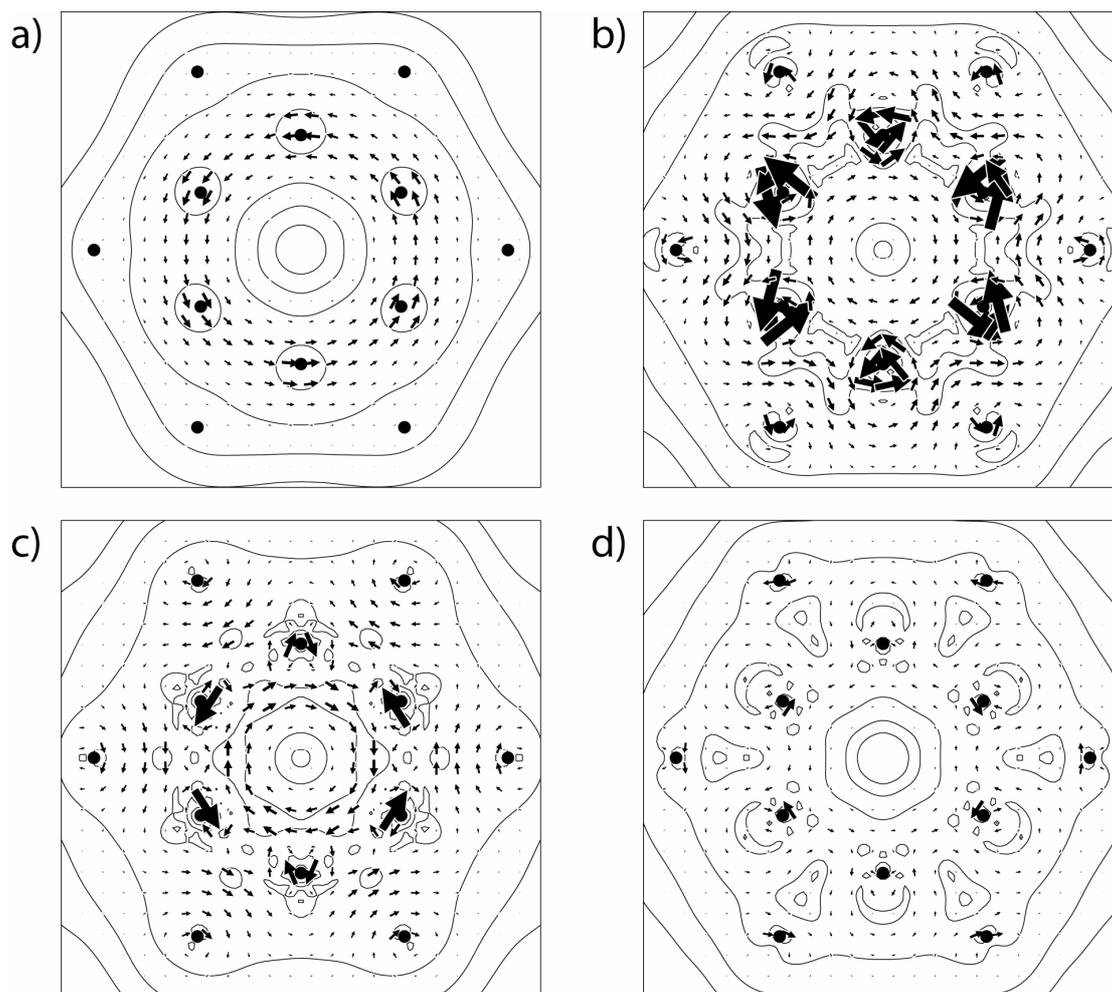
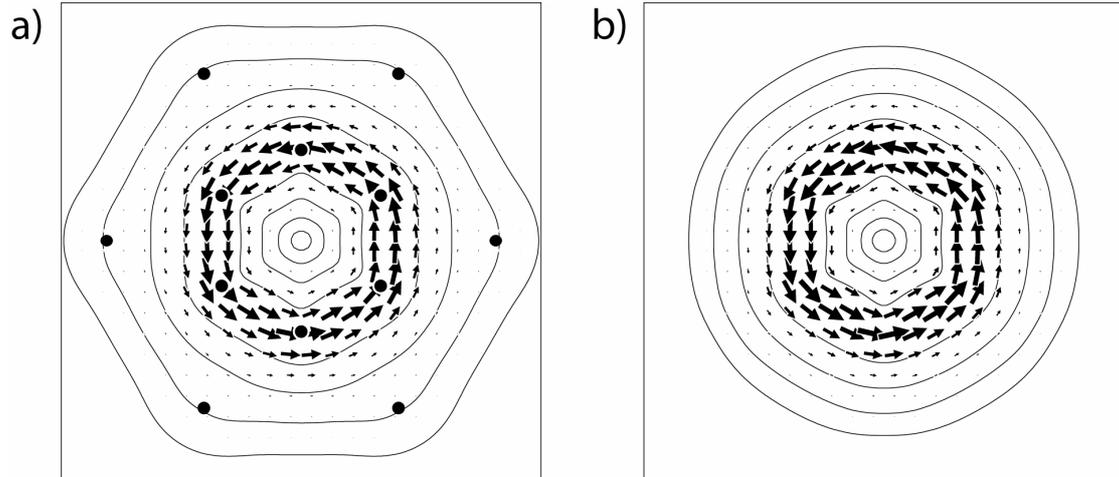


Figure 7



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Figure 8

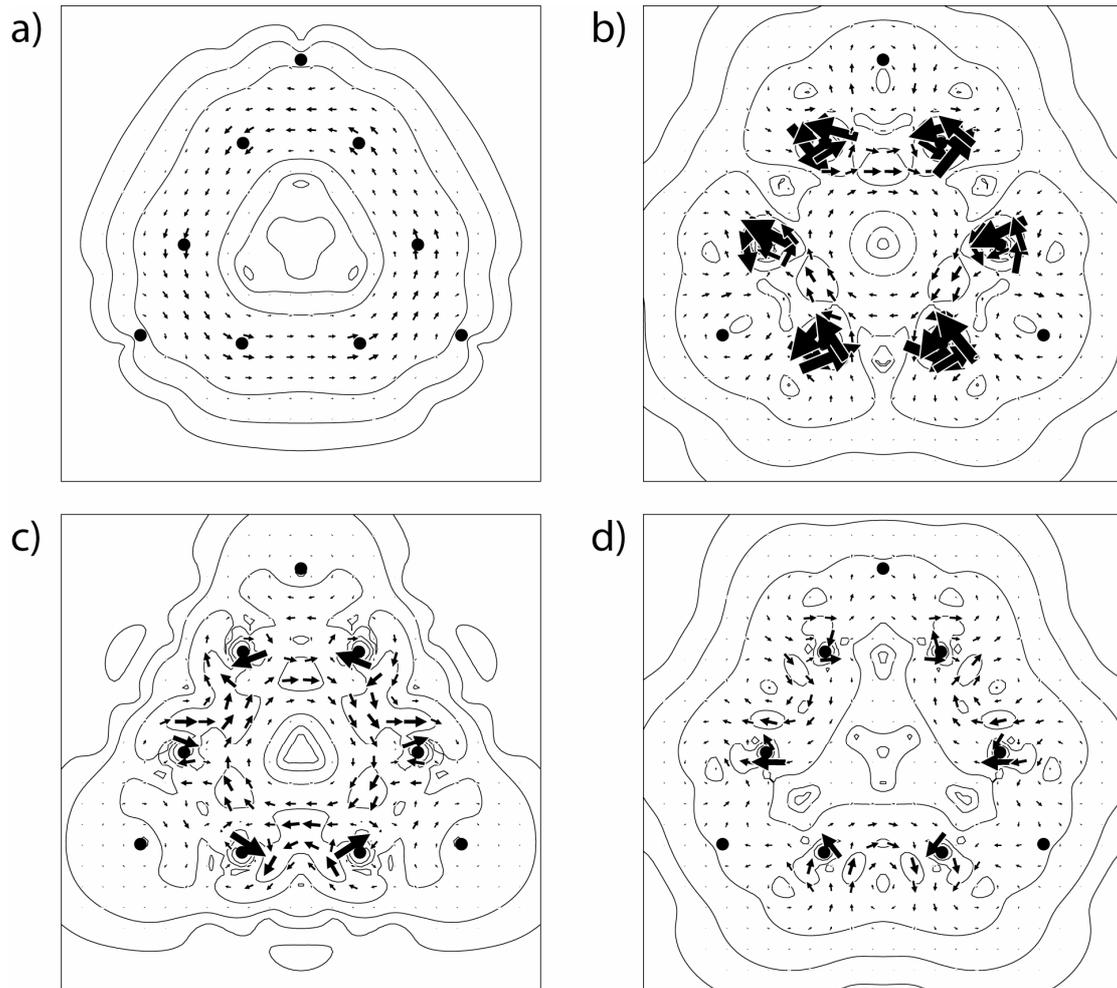
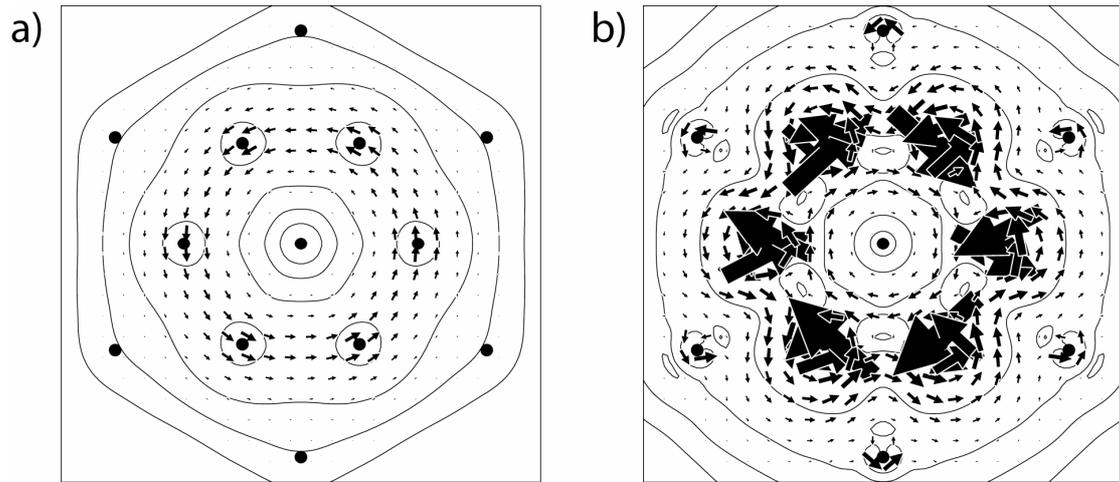
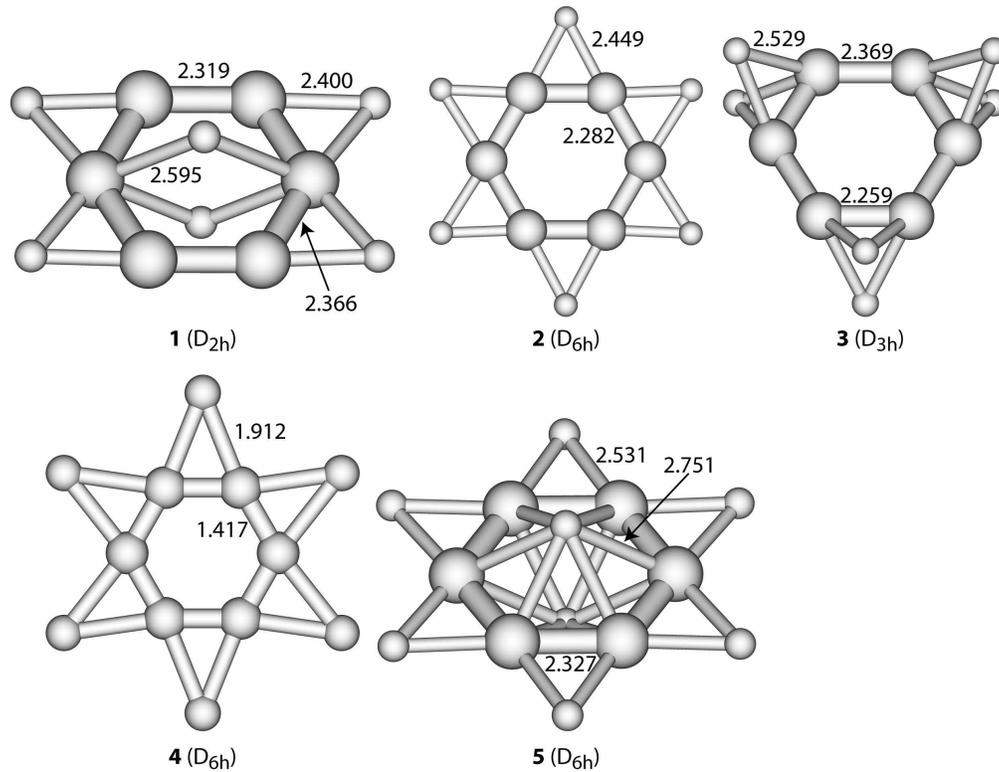


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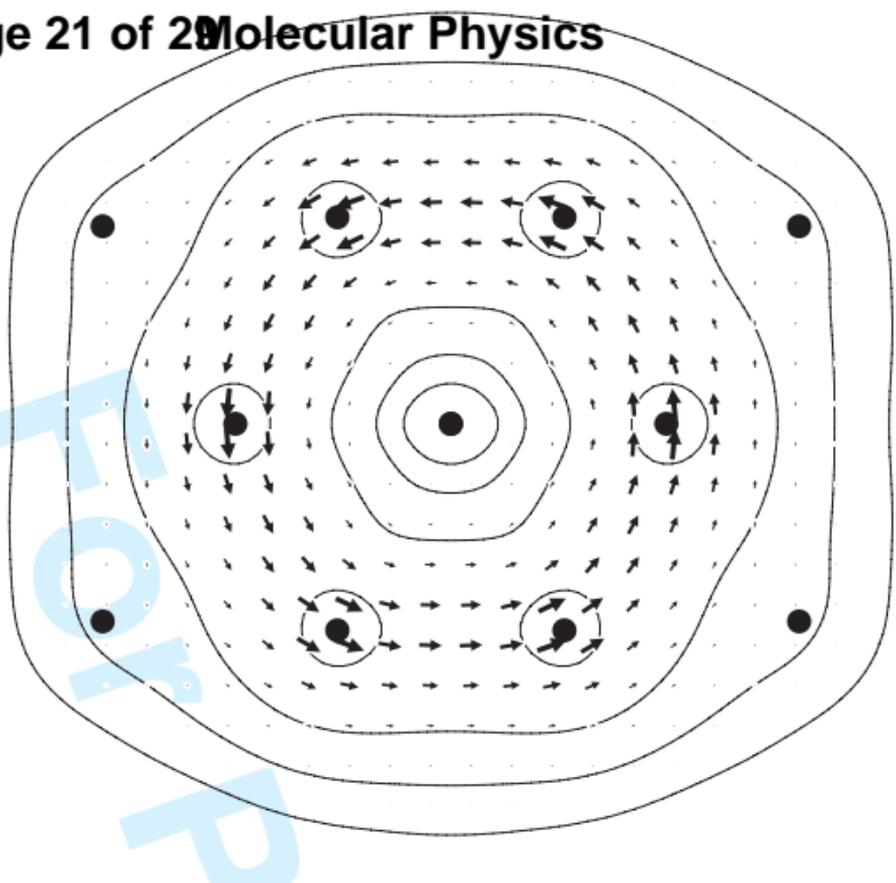


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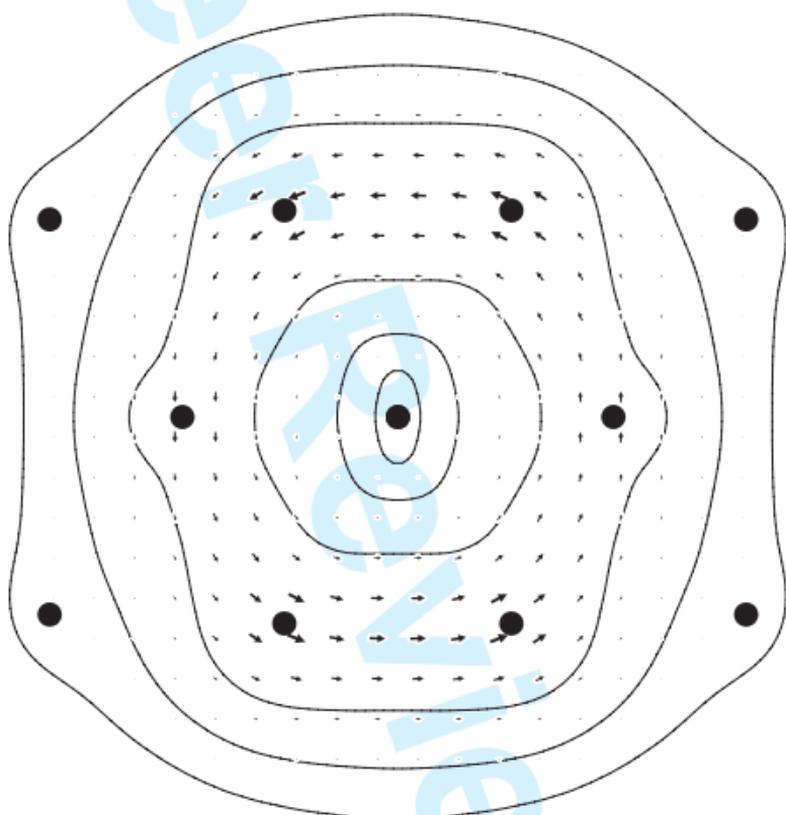
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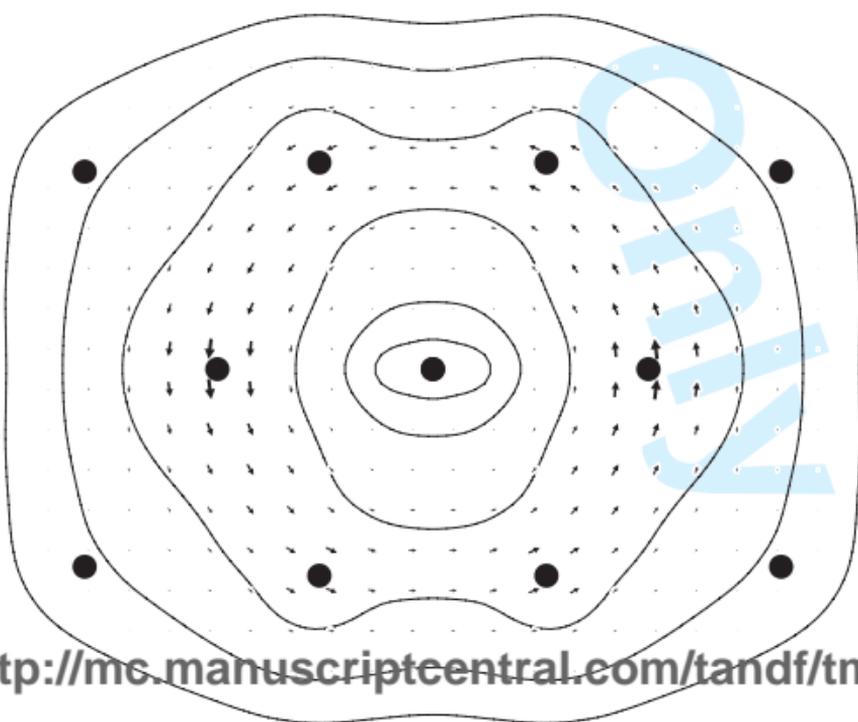
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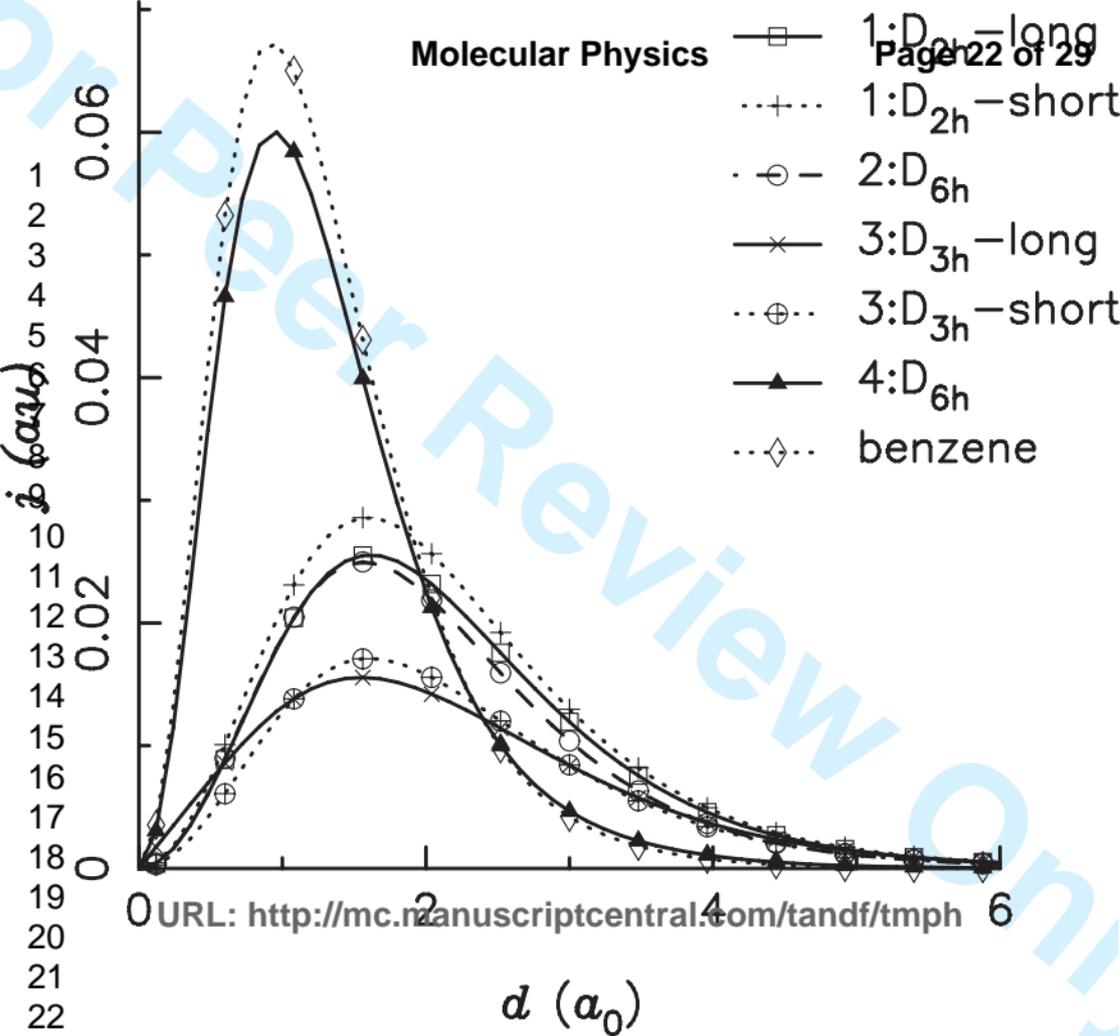
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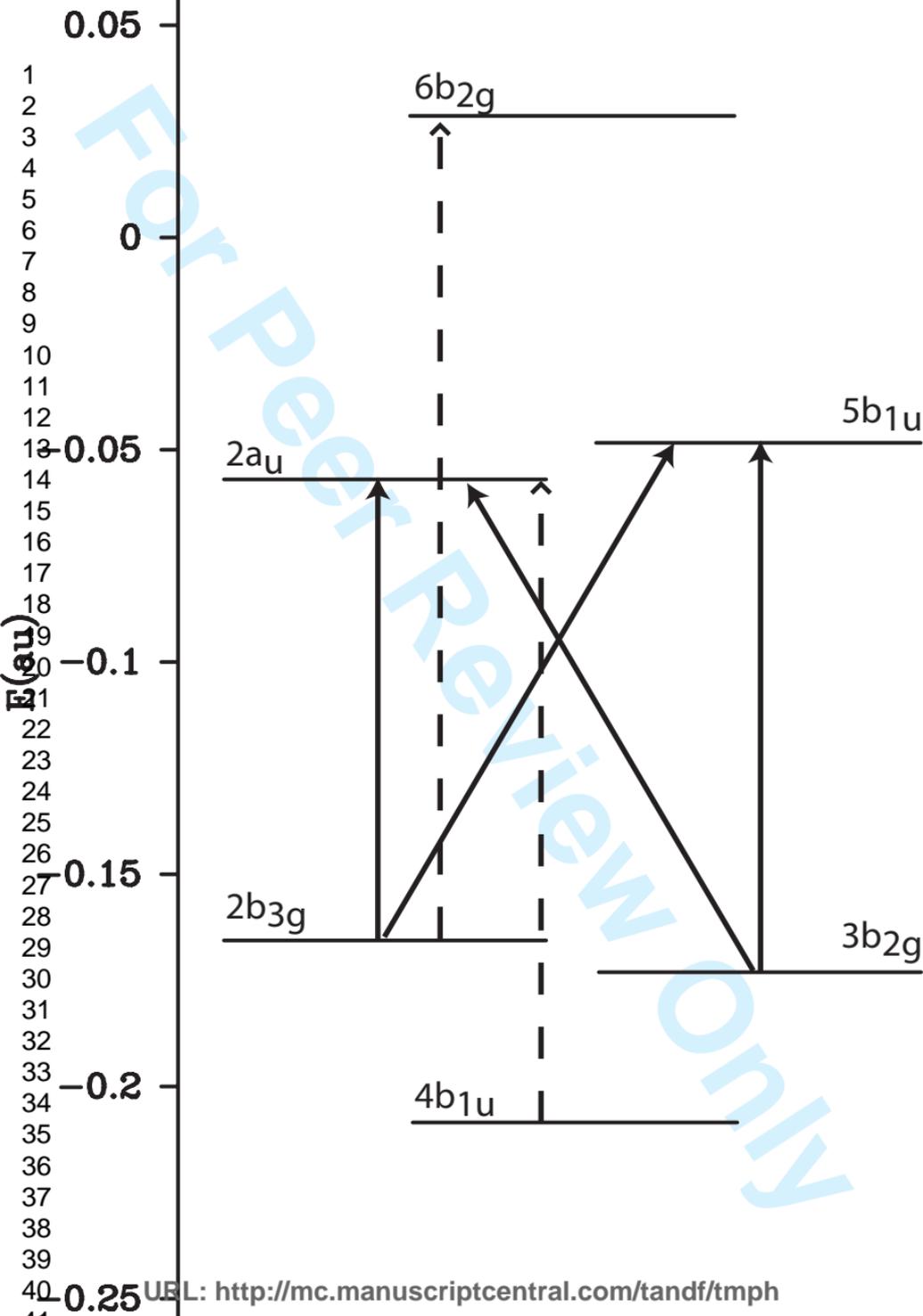


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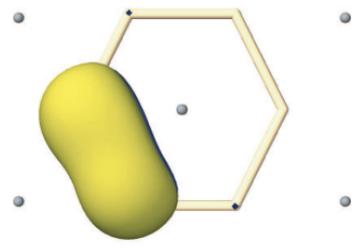
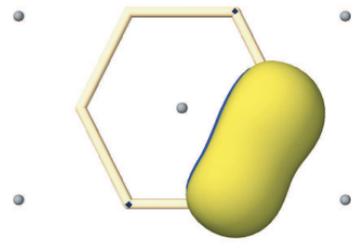
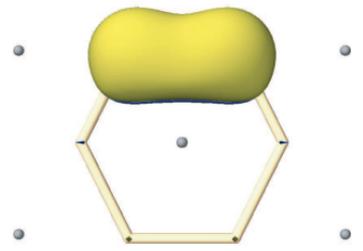
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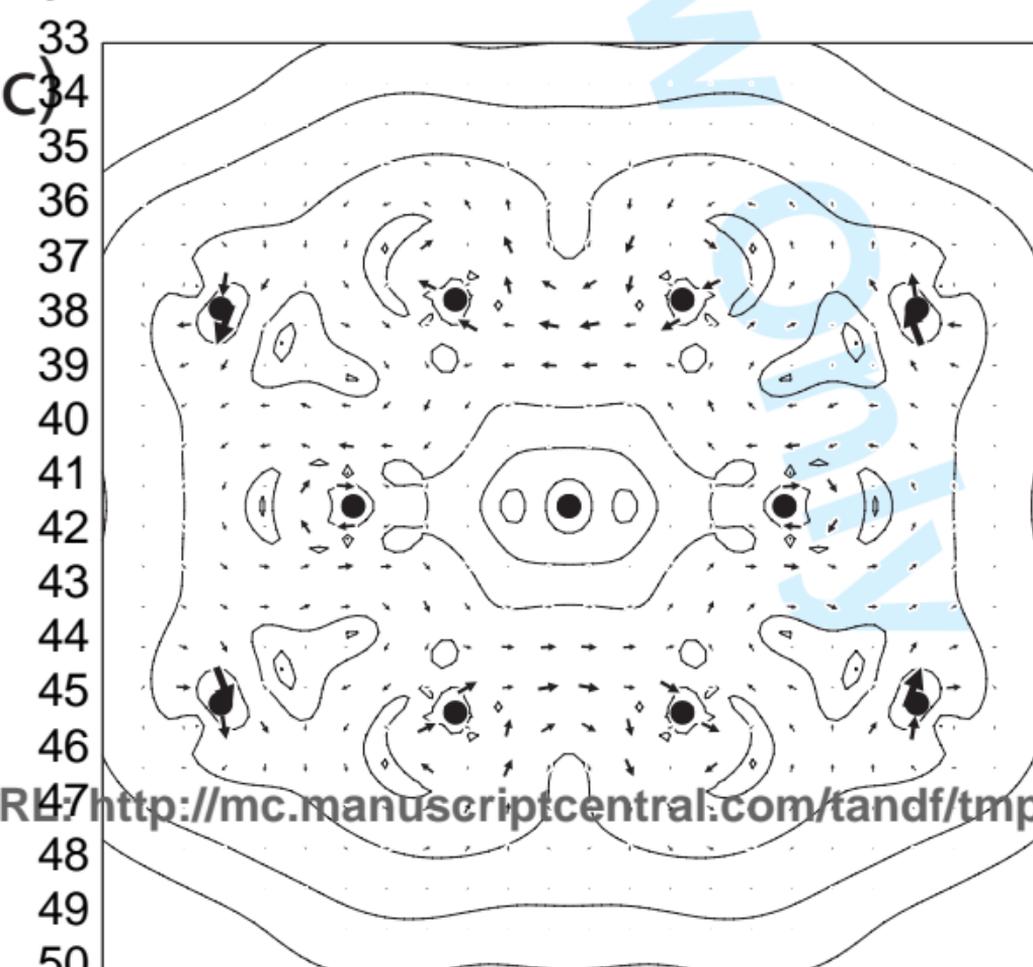
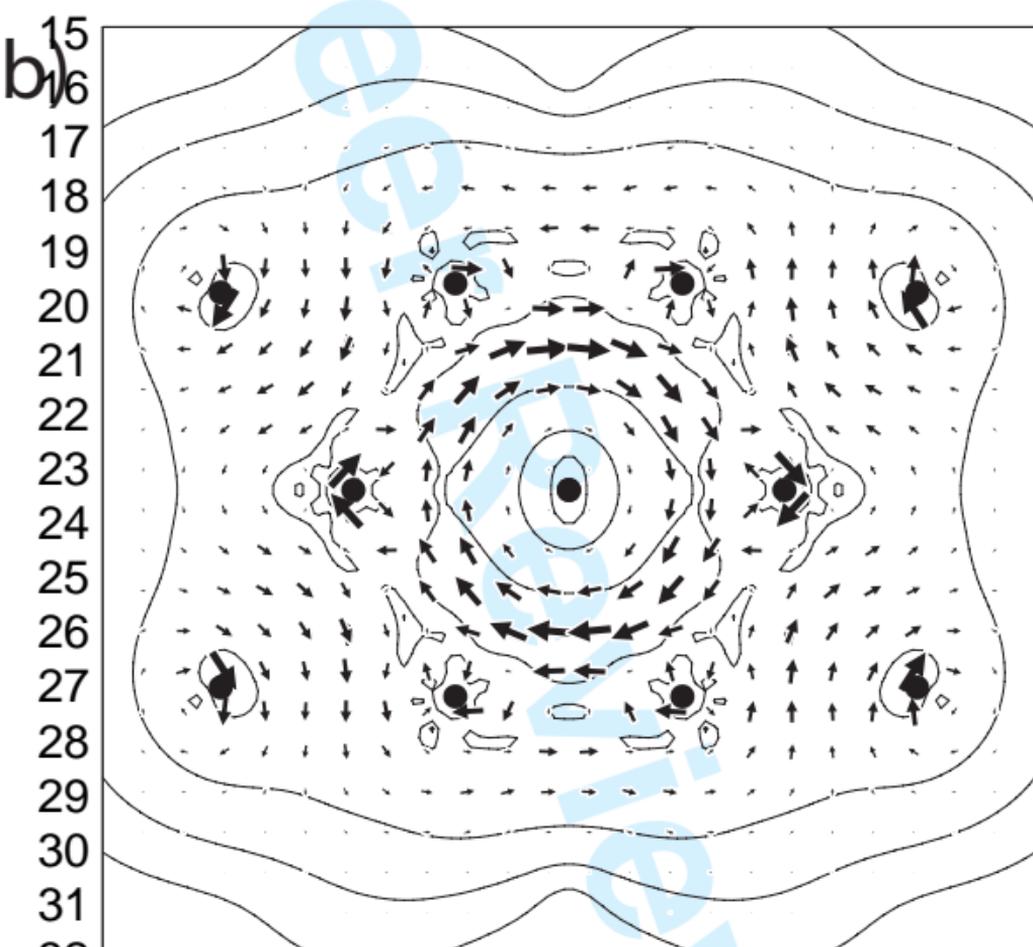
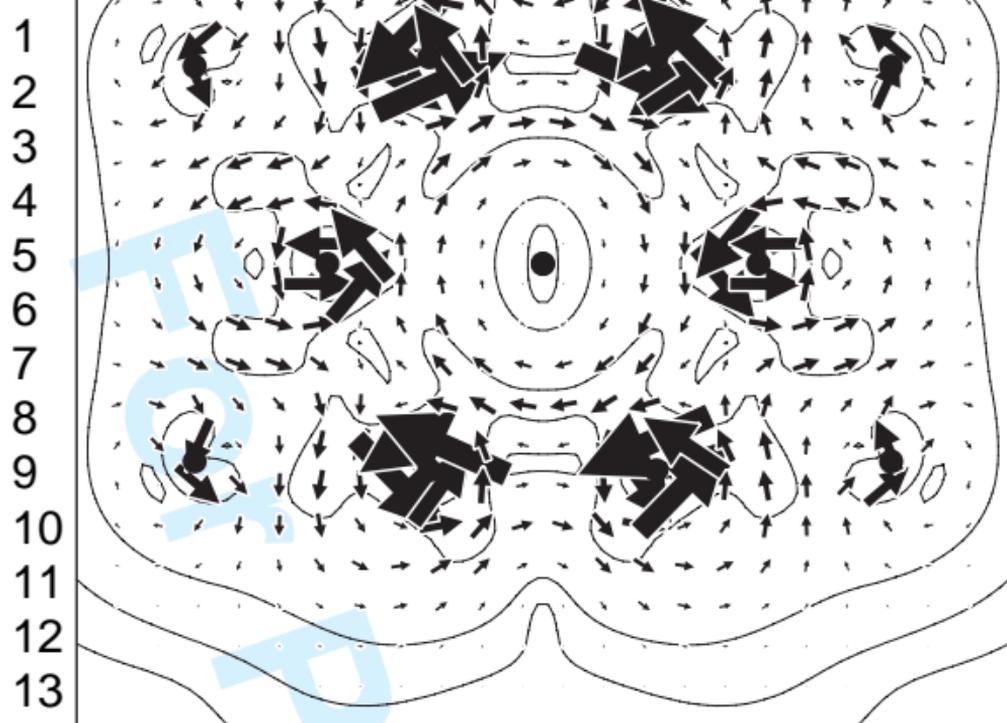
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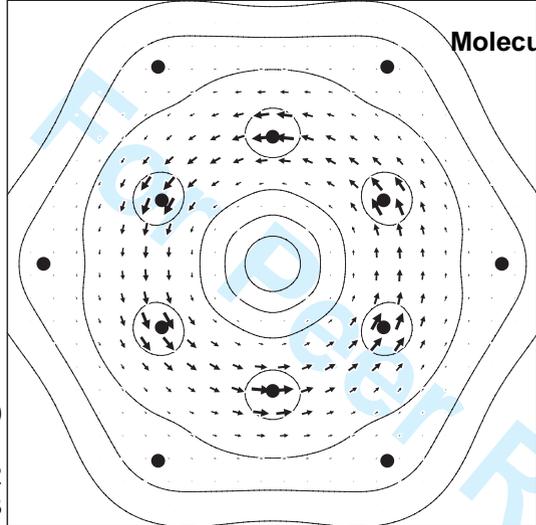




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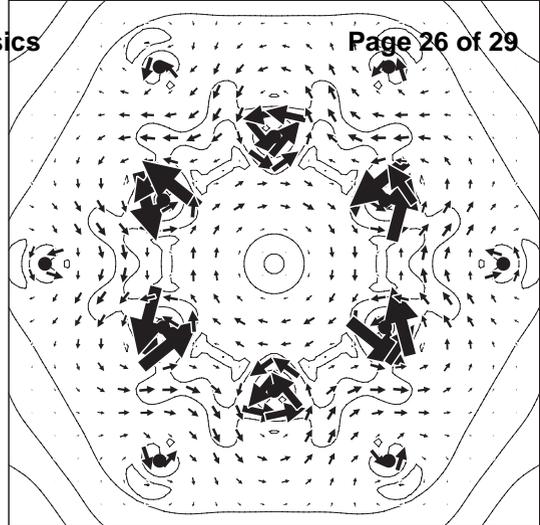
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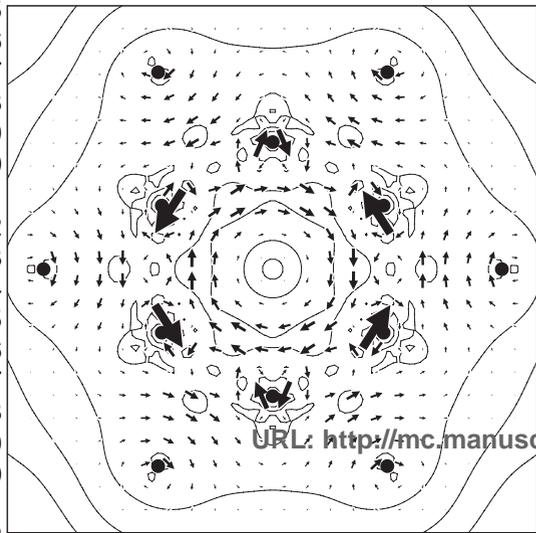


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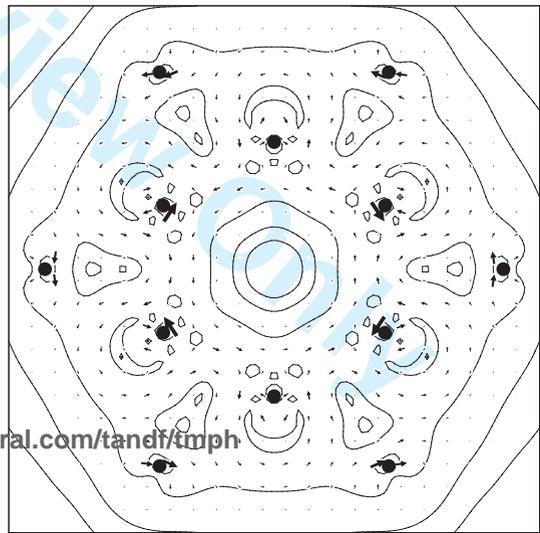
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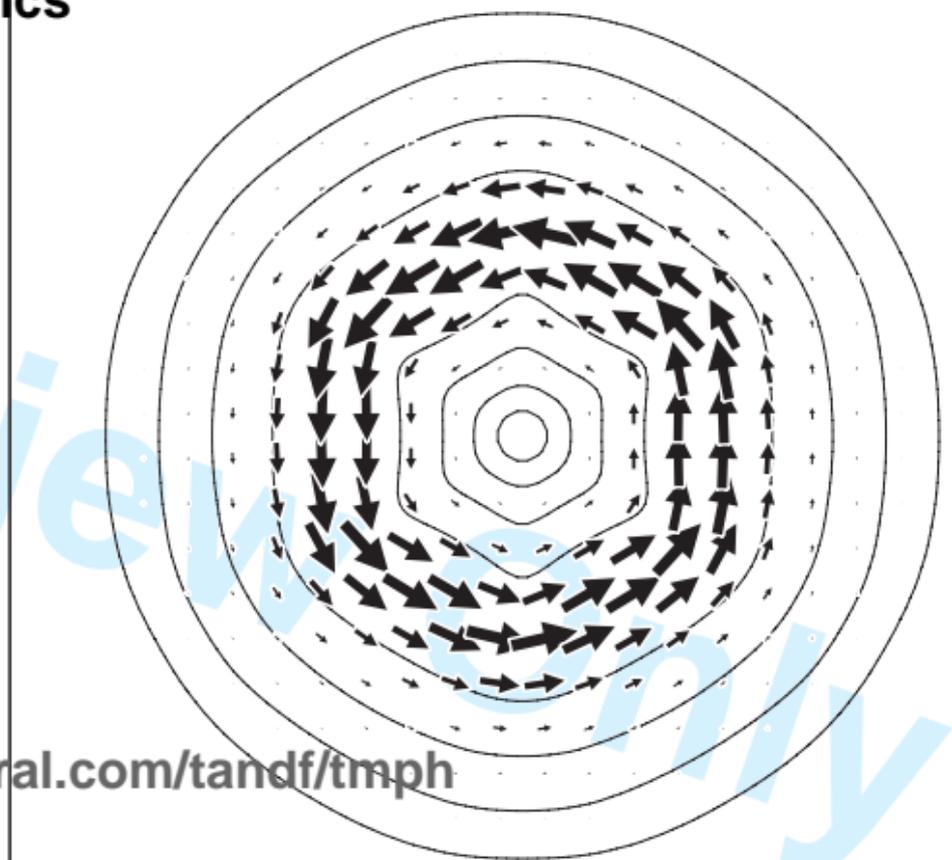
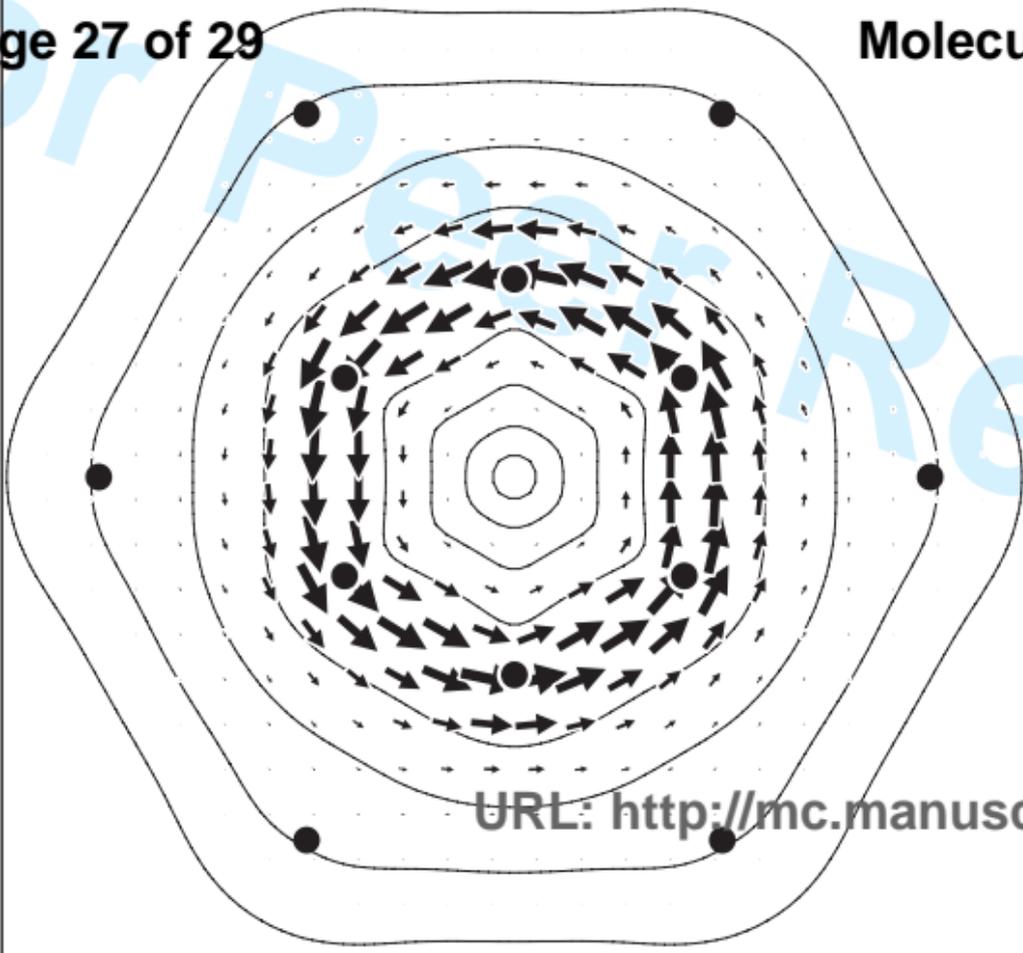
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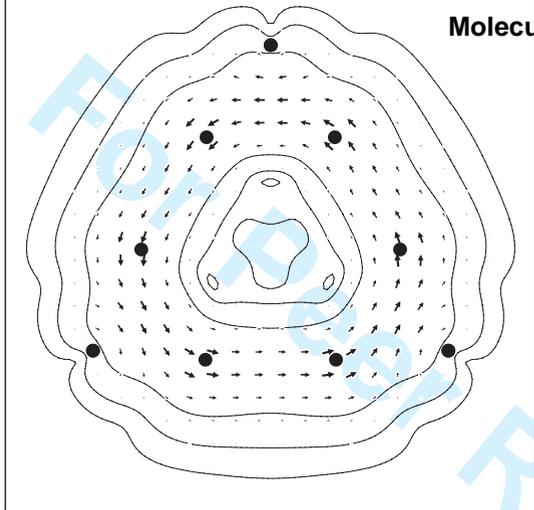
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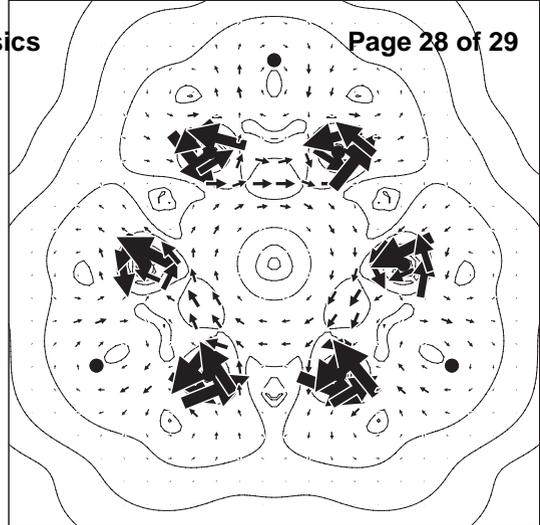
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Molecular Physics

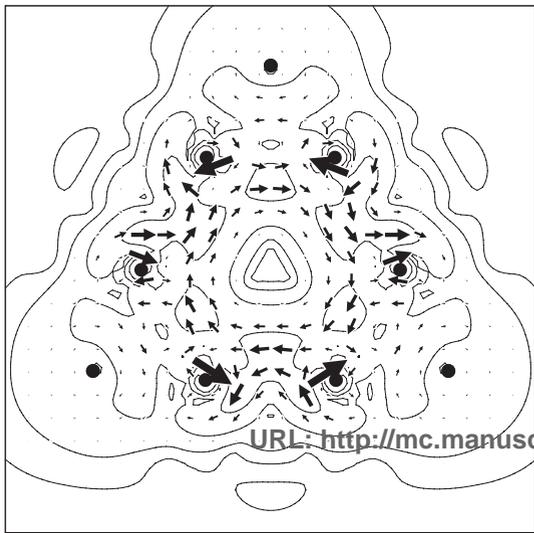
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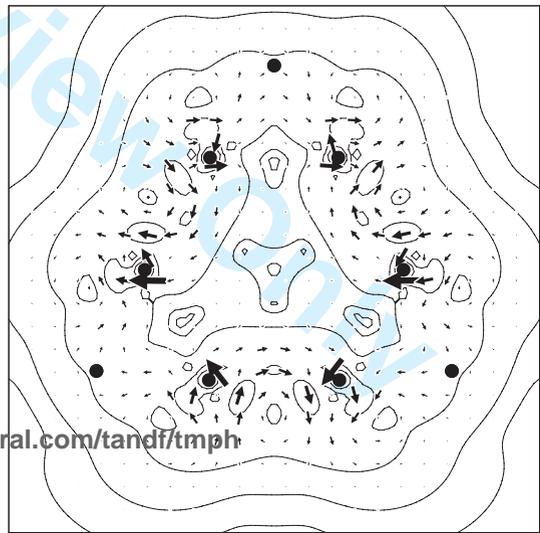
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