

# Using Spartan to Enhance the Student's Understanding of Crystal Field Splitting Diagrams

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**Abstract:** Through the use of Spartan, single-point calculations are performed on a series of germanium hydrides with linear, tetrahedral, square-planar, trigonal-bipyramidal, and octahedral geometries. The hydrogen atoms, representing ligands, are placed sufficiently far away from the central metal so that the covalent bond between the hydrogen and the metal atom is weak. For each structure, the five surfaces that describe the d orbitals on the heavy-metal atom are displayed. Through inspection of how much each of the d orbitals interacts with the ligands and answering a series of critical-thinking questions, the student is guided to understand which crystal field splitting diagram corresponds with each of the five common complex ion geometries.

## Introduction

Crystal field theory is taught by many instructors of general chemistry because it helps their students understand the origin of color in transition metal complexes as well as the paramagnetism of complexes (or lack thereof). If crystal field theory is to be taught to students of general chemistry, a reasonable goal is for the student to obtain an understanding of the origin of splitting patterns of d orbitals in ligand fields of various geometries. Fairly often, textbooks of general chemistry will provide figures representing (1) the d orbitals of a central transition metal, (2) the coordination of ligands' orbitals (but seldom ever more than in an octahedral field), and (3) the splitting patterns of d orbitals in octahedral, tetrahedral, and square-planar fields of ligands [1–7]. Unfortunately, it is rare to see figures that simultaneously illustrate the d orbitals of the metal associated with the regions of charge of the ligands, and even then the student is presented with a static, two-dimensional figure that requires a considerable amount of imagination to fully understand how the d orbitals interact with the ligands' orbitals. What is likely to happen is that the student will forego the analysis of the figures of d orbitals and ligands and “skip to the chase” by memorizing the splitting patterns of the d orbitals.

Because the student's educational resources are limited, the student may never learn why the splitting patterns for transition metals in different ligand field geometries are the way that they are. It would be ideal to have manipulatives (i.e., actual plastic models of each of the d orbitals in each of the ligand fields) for the student to inspect how each metal d orbital interacts with the ligands' orbitals. But one can only imagine how these three-dimensional models would be constructed. In addition, to purchase enough of the models so that everyone in the classroom would have the opportunity to inspect them in the time period of the class would carry a hefty price tag.

The computational chemistry software package Spartan [8], however, is now “one of the leading chemical education molecular modeling tools” [9]. This paper presents how

Spartan may be used to simultaneously display the d orbitals of a central (heavy) metal atom (namely, germanium) and “ligands” (hydrogen atoms) in fields of various geometries. For this application of Spartan, the hydrogen atoms are bound covalently to the central germanium at a sufficient distance so that the displayed images accurately (both in shape and relative orientation) depict the d orbitals that they represent. The student may open one structure or may have more than one structure on the screen at a time for the purpose of comparison. One “surface” (the molecular orbital representing a d orbital) may be activated, or (if the student likes) more than one surface may be inspected simultaneously for a given structure. Students may click and drag with the mouse to rotate the image on the computer screen so that they may see how each of the lobes of every d orbital interacts with each ligand. Through a series of questions, the student is guided to an understanding of the amount of interaction that each d orbital has with the ligand orbitals in a given geometry. Then, the student determines which of the given d-orbital splitting patterns corresponds to the tetrahedral, the square-planar, and the octahedral complex. The ambitious teacher may also wish to cover linear and trigonal-bipyramidal complexes as well, because they are fairly common; therefore, these models are included in this paper as well.

## Implementation and Discussion

Unless the students are already familiar with performing computations using Spartan, it is recommended that the single-point calculations with selected surfaces (see Table 1) be performed ahead of time by the course instructor and saved before class begins. For all the structures generated in this study (a) germanium was used for the central transition metal and hydrogen atoms were used for the peripheral ligands, (b) the Ge–H bond lengths were set to 1.600 Å, (c) single-point density-functional calculations using the pBP/DN\* basis set were performed using PC Spartan Pro [10], and (d) only five

**Table 1.** The d Orbitals and Corresponding Surfaces for Each Complex

Complex	$d_{xy}$	$d_{xz}$	$d_{yz}$	$d_{x^2-y^2}$	$d_{z^2}$
$\text{GeH}_2^{2+}$	HOMO-5	HOMO-3	HOMO-4	HOMO-6	HOMO-2
$\text{GeH}_4 (T_d)$	HOMO-6	HOMO-8	HOMO-7	HOMO-4	HOMO-5
$\text{GeH}_4 (D_{4h})$	HOMO-5	HOMO-7	HOMO-6	HOMO-4	HOMO-8
$\text{GeH}_5^-$	HOMO-8	HOMO-5	HOMO-6	HOMO-9	HOMO-7
$\text{GeH}_6^{2-}$	HOMO-8	HOMO-7	HOMO-6	HOMO-10	HOMO-9

surfaces (molecular orbitals) need to be set up to be displayed. (See Table 1 and the supporting information.)

The germanium hydride series is meant to represent a generic transition metal in a variety of ligand fields. Hydrogen (contributing only one electron) was chosen as the ligand in order to minimize how much the set of ligands would define the molecular orbitals and, therefore, the displayed surfaces that were to represent “pure” d orbitals. Germanium was chosen as the central metal because (1) it has occupied d orbitals in the ground state; (2) it is a metal; and (3) it is chemically reasonable that germanium covalently bonds to 2, 4, 5, or 6 hydrogen atoms to form linear, tetrahedral, square-planar, trigonal-bipyramidal, or octahedral species, respectively. It is also aesthetically pleasing that both germanium as the generic central metal and hydrogen as the generic ligands appear in grey scale while the d orbitals appear in vibrant blue and red hues.

When a germanium hydride is constructed in Spartan, the Ge–H bond starts off being 1.525 Å long. Chlorogermane and trichlorogermane have Ge–H bond lengths of 1.52 Å and 1.55 Å, respectively [11]; so, presumably, a bond length of 1.525 Å would result in significant amount of overlap between the orbitals of germanium and the 1s orbitals of the hydrogen atoms to form covalent bonds. The bond lengths were increased to 1.6 Å in order to avoid any visible overlap between the d orbitals of the germanium and the 1s orbitals of the hydrogen atoms in the displayed surfaces. A bond length longer than 1.6 Å was not used in order to keep the ligands as close as possible to the displayed d orbitals. This should allow the student to more easily see which d orbitals interact more than others with the ligands.

While the Hartree–Fock method using a minimal basis set was optimal (primarily for ease in interpreting the output molecular orbital wavefunctions), the density-functional method using the pBP/DN\* basis set was chosen because it worked consistently for all of the structures and yielded the nicest visible results. The optional boxes for “Print: Orbitals & Energies,” “Symmetry,” and “Apply Globally,” should be checked in the Setup Calculations dialog box. The multiplicity of each substance is to be a singlet. The total charges of  $\text{GeH}_2$ ,  $\text{GeH}_5$ , and  $\text{GeH}_6$  are “Dication,” “Anion,” and “Dianion,” respectively. While these charges are not absolutely necessary, the total charge and multiplicity of a species must agree for the calculation to run successfully. The surfaces to be set up for each of the species are given in Table 1. (The labels of the d orbitals are likely to be different if one uses a different basis set. The surfaces of degenerate d orbitals might be swapped, even if the pBP/DN\* basis set is used.)

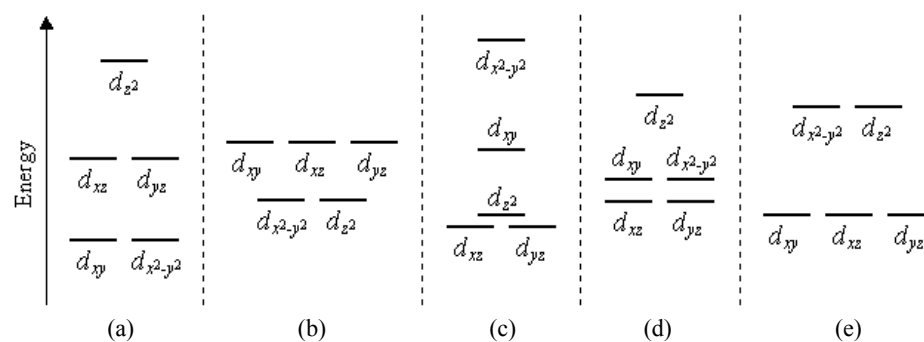
The surfaces representing the d orbitals for the linear, the square-planar, the trigonal-bipyramidal, and the octahedral complexes can be calculated in more-or-less the same manner. First, the species is built (using the “Expert” menu of the “Add Fragment” dialog screen of Spartan). If the point group of the

species is incorrect, a simple MMFF minimization (i.e., by clicking on the icon with an arrow pointing down toward an E) of the structure will correct it. Then the bond lengths are each made to be 1.600 Å. The surfaces (according to Table 1) are then set up. (In order to minimize confusion on the part of the student, it is recommended that for each structure the order in which the surfaces are added to the “Surface List” is  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$ , and lastly  $d_{z^2}$ .) Then, the single-point DFT (pBP/DN\*) calculation is set up and submitted. (The square-planar complex must be submitted a second time to overcome an error. Because the rms density converges to an unreasonably low value after 40 iterations of the single-point calculation of square-planar  $\text{GeH}_4$ , the SCF convergence is considered to be poor and the calculation ends in an error. This error should be ignored and the single-point calculation may simply be submitted a second time. When it completes, appropriately appearing surfaces may be displayed.) The tetrahedral complex, however, must be handled in a different manner if the surfaces are to have the appropriate shapes and relative orientations with respect to the ligands so that the student will be able to correctly predict the d orbitals’ relative energies. Further reading about how the appropriate surfaces of tetrahedral  $\text{GeH}_4$  were calculated may be found in the supporting materials included with this paper.

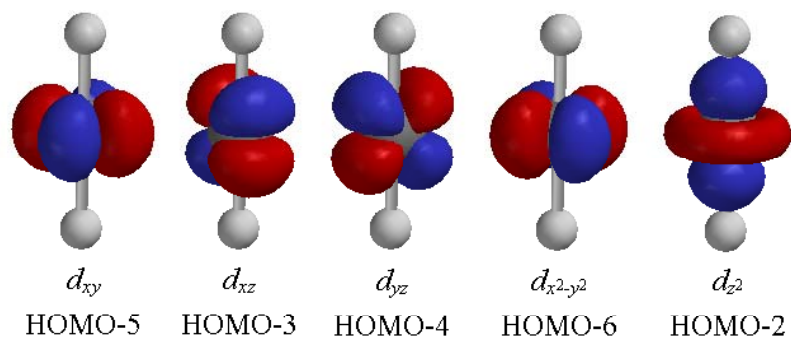
The students are presented with the d-orbital splitting patterns shown in Figure 1. The patterns may each be presented on a separate card so that they are not in any particular order. The relative energies of the d orbitals in each splitting pattern are based on Table 11.5 of Huheey, Keiter, and Keiter [12], but students need not concern themselves with the actual values, just which d orbitals have more, less, or the same energy as other orbitals.

Assuming the calculations of the structures have already been performed by the instructor before class, the students then open the appropriate files (perhaps one at a time). The surfaces (again, one at a time) are displayed. A legend is provided so that the student knows which d orbital is represented by each surface (e.g., that “HOMO-8” represents the  $d_{xy}$  orbital in the octahedral complex). It is recommended that the surfaces be ordered  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$  from top to bottom in each “Surface List” for each complex so as to minimize confusion. (For example, when the surfaces are added for the octahedral structure, they are added in the following order: “HOMO-8,” “HOMO-7,” “HOMO-6,” “HOMO-10,” and lastly “HOMO-9” according to Table 1.) Otherwise, Table 1 should be provided to the students. By clicking and dragging with the computer mouse, the view of the structure can be adjusted by students so that they can gauge relatively how much each d orbital interacts with the ligands. Figures 2 (linear geometry) through 6 (octahedral geometry) show each species in a given orientation (in general, with the z axis going up on the page, the y axis going to the right, and the x axis coming out of the page) with the five d orbitals. It should be noted that when the orientation of a structure is rotated (within Spartan), a better view of how a d orbital interacts with an obscured ligand can be obtained.

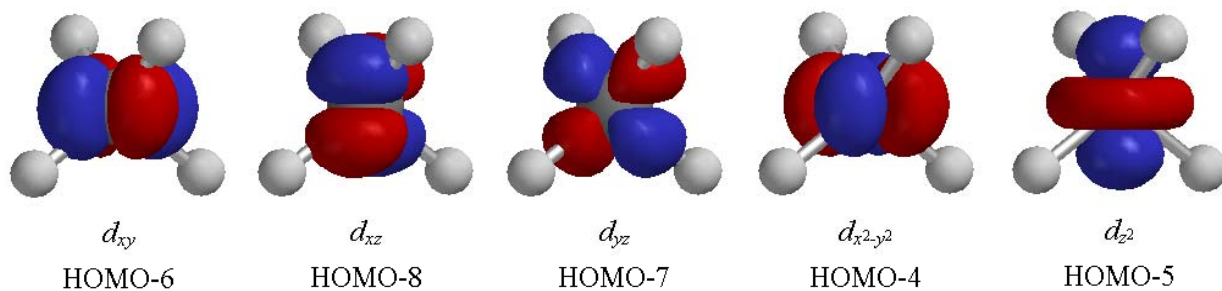
After the student has used Spartan to inspect how the d orbitals interact with the ligands in a given geometry, the student can then be guided to determine which of the splitting diagrams (Figure 1) corresponds to that geometry as follows: (1) By the time that the student is to be taught about crystal field theory, it is likely that the student will have worked out a number of examples of electron configurations of transition



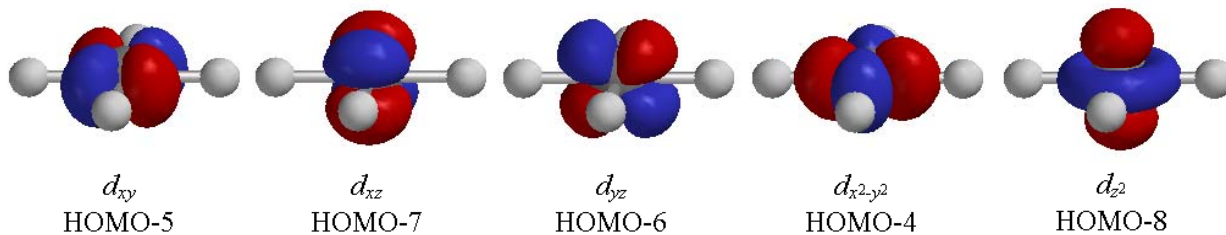
**Figure 1.** Splitting patterns of d orbitals in ligand fields for (a) linear  $ML_2$ , (b) tetrahedral  $ML_4$ , (c) square-planar  $ML_4$ , (d) trigonal-bipyramidal  $ML_5$ , and (e) octahedral  $ML_6$ .



**Figure 2.** The surfaces and the corresponding d orbitals on Ge in  $GeH_2^{2+}$ .



**Figure 3.** The surfaces and the corresponding d orbitals on Ge in tetrahedral  $GeH_4$ .



**Figure 4.** The surfaces and the corresponding d orbitals on Ge in square-planar  $GeH_4$ .

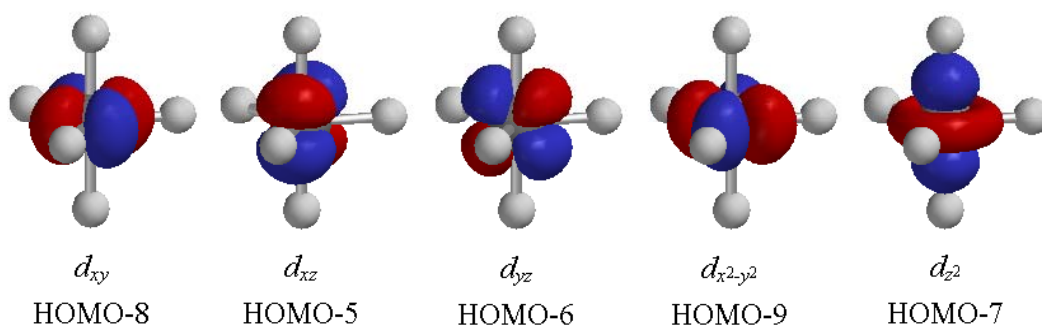


Figure 5. The surfaces and the corresponding d orbitals on Ge in trigonal-bipyramidal  $\text{GeH}_5^-$ .

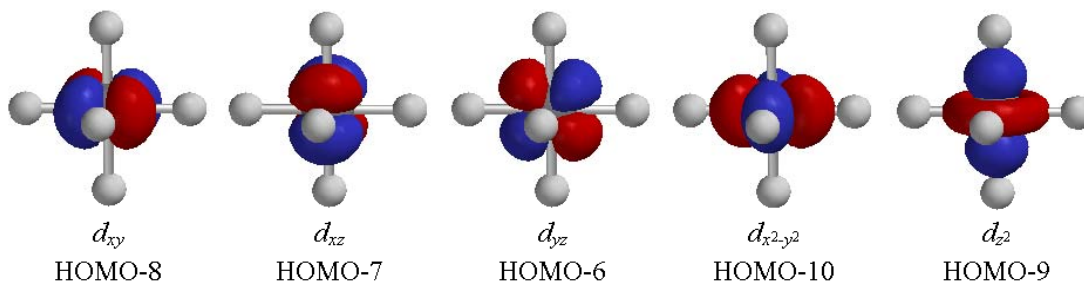


Figure 6. The surfaces and the corresponding d orbitals on Ge in octahedral  $\text{GeH}_6^{2-}$ .

metals that are part of complexes, but it would be wise to remind the student that the central metal does have a number of electrons in its d orbitals. (2) The student should also be reminded that the ligands have excess electron density that is being donated to the metal. (3) The student should be reminded of Coulomb's law and asked what kind of force (attractive or repulsive) like-charged particles experience when they are brought near each other. (4) The student should be led to the conclusion that because the metal's d orbitals are populated with electrons and because the ligands' orbitals have electrons, the d orbitals that interact most strongly with the ligands will experience the greatest repulsive force. (5) Finally, the student should be reminded that the d orbitals of an isolated metal atom have the same amount of energy. The student can be led to the understanding that once the d orbitals are exposed to a field of ligands, all of the d orbitals will be elevated in energy because the electrons in the d orbitals and the electrons in the ligand orbitals repel each other, but the student must make the final connection that those d orbitals that interact to the greatest extent with the ligands will end up having the greatest energy. Once the student has made this connection, ranking of the d orbitals in terms of how much they interact with the ligands (and keeping the d orbital designations in mind) will allow the student to determine which splitting pattern belongs to particular ligand field geometry.

### Analysis of Spartan Surfaces

Students will perhaps remember from an earlier general chemistry class (for example, in which they learned about molecular orbital theory) that strong bonds and a more stable system result from significant orbital overlap between bound atoms; therefore, in order to guide the students to an understanding of the relative energies of d orbitals in the various geometries of ligand fields, the students probably ought to be made aware that bonding in crystal field theory is

based on electrostatics. To this end, the students may be asked questions such as the following:

1. There are likely to be electrons in the d orbitals of the central metal atom and in the orbitals of the ligands surrounding the metal.
  - a. Do electrons attract or repel each other? (You may circle your answer.)
  - b. Which of the following statements is TRUE? (You may circle your answer.)
    - i. When a negatively charged particle is brought close to another negatively-charged particle, the system becomes stabilized (i.e., the energy of the system decreases).
    - ii. When a negatively charged particle is brought close to another negatively charged particle, the system becomes destabilized (i.e., the energy of the system increases).
  - c. When the orbitals of the ligands get close to the d orbitals of the central metal atom, which of the following d orbitals will become more destabilized? (You may circle your answer.)
    - i. the d orbitals that more efficiently overlap with the orbitals of the incoming ligands
    - ii. the d orbitals that less efficiently overlap with the orbitals of the incoming ligands

2. For each of the complexes of the various geometries, one complex ion at a time: (1) open its Spartan file; and (2) display each d orbital, one at a time, noting and keeping a log of which d orbitals interact more with the "ligands" and which d orbitals interact to the same extent as others.

When the student inspects the surfaces of  $\text{GeH}_2^{2+}$  (Figure 2), the student should notice that (1)  $d_{z^2}$  interacts the most with the ligands and (2)  $d_{xz}$  and  $d_{yz}$  are symmetrically equivalent and interact with the ligands a little more than  $d_{xy}$  and  $d_{x^2-y^2}$ , which are themselves symmetrically equivalent. With this in mind,

the student should be able to determine that splitting pattern (a) in Figure 1 corresponds to a linear complex.

When the student inspects the surfaces of tetrahedral  $\text{GeH}_4$  (Figure 3), the student should see that (1)  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  are symmetrically equivalent and that in each orbital each lobe is partially directed at a ligand and (2)  $d_{x^2-y^2}$  and  $d_{z^2}$  have no lobes directed at any ligand, which makes them lower in energy. The student should, therefore, be able to determine that the splitting pattern (b) in Figure 1 corresponds to a tetrahedral complex.

When the student inspects the surfaces of square-planar  $\text{GeH}_4$  (Figure 4), the student should see that (1)  $d_{xz}$  and  $d_{yz}$  are symmetrically equivalent, and their lobes are not directed at any of the ligands, which makes them low in energy; (2) all four of the lobes of  $d_{xy}$  are in the same plane as the ligands, so  $d_{xy}$  is higher in energy than  $d_{xz}$  and  $d_{yz}$ ; (3) the torus of  $d_{z^2}$  is in the same plane as the ligands, so  $d_{z^2}$  is higher in energy than  $d_{xz}$  and  $d_{yz}$ ; and (4) all four lobes of  $d_{x^2-y^2}$  are directed towards the ligands, which makes it the highest in energy. Thus, the student should be able to determine that splitting pattern (c) in Figure 1 corresponds to a square-planar complex.

When the student inspects the surfaces of  $\text{GeH}_5^-$  (Figure 5), the student should notice that (1)  $d_{z^2}$  interacts the most with the ligands; (2) the lobes of  $d_{xz}$  and  $d_{yz}$  are not directed toward any of the ligands, which makes them low in energy; and (3) the equatorial ligands are in the same plane as  $d_{xy}$  and  $d_{x^2-y^2}$ , and their lobes are partially directed toward the ligands, which makes them higher in energy than  $d_{xz}$  and  $d_{yz}$ . Thus, the student should be able to determine that splitting pattern (d) in Figure 1 corresponds to a trigonal-bipyramidal complex.

When the student inspects the surfaces of  $\text{GeH}_6^{2-}$  (Figure 6), the student should notice that (1)  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  are symmetrically equivalent, and the lobes of each orbital are not directed at any ligand, which makes them low in energy; (2) all four lobes of  $d_{x^2-y^2}$  are directed towards four of the ligands, which makes it high in energy; and (3) the axial lobes of  $d_{z^2}$  are directed towards two of the ligands and the torus is in the same plane as the other four ligands, which makes it high in energy. The student should, therefore, be able to determine that splitting pattern (e) in Figure 1 corresponds to an octahedral complex.

## Conclusion

The single-point density-functional calculations of  $\text{GeH}_2^{2+}$ , square-planar  $\text{GeH}_4$ ,  $\text{GeH}_5^-$ , and  $\text{GeH}_6^{2-}$  are easy to perform using Spartan. The Spartan input file for tetrahedral  $\text{GeH}_4$  requires just a few modifications for the surfaces representing appropriately oriented d orbitals on the germanium atom to be displayed. By activating the surfaces and clicking and dragging the image with the mouse, the student can visualize each of the five d orbitals ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$ ) in their proper relative orientations in three-dimensional space. For each

germanium hydride, when the d orbitals of the germanium atom are inspected in relation to the positions of the hydrogen atom "ligands," the student may be guided to predict which d orbitals are more destabilized than other d orbitals. Thus, instead of merely memorizing the splitting patterns, the student learns why the d-orbital splitting diagrams for a transition metal are the way they are displayed in their textbook for tetrahedral, square-planar, and octahedral ligand complexes. The splitting diagrams of linear and trigonal-bipyramidal complexes (common geometries, which are essentially never covered in the crystal field theory section of general chemistry textbooks) may also be investigated employing geometry and Coulomb's law, which provides the student with additional practice in assessing the relative energies of orbitals.

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**Supporting Materials.** Supporting materials are available in a Zip file (<http://dx.doi.org/10.1333/s00897050866a>)

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