CHEM106: Assignment 9

Hydrogen Molecule

1. Set up the Schrödinger equation for the H2+ ion.

To establish the Schrödinger equation for a given system, we need to figure out the Hamiltonian,, which is the total energy operator formed by combining the kinetic energy operator with the potential energy operator . For the H2+ ion,

the Hamiltonian (in atomic units) is defined by

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where 

represents the Laplacian operator. In the Hamiltonian, the first two terms are the kinetic energy operators for the nucleus A and B; the third term is the kinetic energy operator for the electron; the fourth and the fifth terms represent the electrostatic attraction between the electron and the nucleus A and B, respectively; and the last term accounts for the electrostatic repulsion between the two nuclei.

Thus, the Schrödinger equation for the H2+ ion is

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2. Define the Born-Oppenheimer approximation, and illustrate how it can be applied to solve the Schrödinger equation for the H2+ ion.

In the Born-Oppenheimer approximation, it is assumed that the motion of the atomic nuclei can be neglected when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the mass difference: the mass of an atomic nucleus is much larger than the mass of an electron (more than 1000 times larger). Because of this difference, the nuclei move much more slowly than the electrons and can be considered fixed. It is worth noting that the Born-Oppenheimer approximation is necessary to solve all molecular Schrödinger equations.

Under the Born-Oppenheimer approximation, the molecular Schrödinger equation for the H2+ ion becomes analytically solvable. Starting from the full Hamiltonian (see Prob. 1)

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the Born-Oppenheimer approximation eliminates the kinetic energy operators for the nuclei (first two terms). So the reduced Hamiltonian becomes

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where the last term is simply a constant since the internuclear distance R is fixed.

Thus, the molecular Schrödinger equation for the H2+ ion is reduced to an electronic Schrödinger equation:

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The electronic Schrödinger equation can be solved at various values of R.

3. Bonding of diatomic molecules is described by the molecular orbital theory, in which linear combination of atomic orbitals forms molecular orbitals.

1. Sketch the bonding and antibonding molecular orbitals that are formed when the atomic orbitals listed in the following table are combined.

When molecular orbitals are formed from atomic orbitals, the in-phase superposition of atomic orbitals leads to the bonding orbital. However, the out-of-phase superposition atomic orbitals produce the antibonding orbital.

|  |  |
| --- | --- |
| Atomic orbitals | Bonding orbital\* |
| 2px + 2px |  |
| 2pz  + 2pz | P-orbitals_ZZ+.png |
| Atomic orbitals | Antibonding orbital |
| 2px + 2px |  |
| 2pz  + 2pz | P-orbitals_ZZ-.png |

\*Note: The phase (or sign) of the wave function is color coded. The positive (+) and negative (-) phases are colored as cyan and white, respectively.

1. What makes a bonding orbital?

As shown in part A, the bonding orbital results from the in-phase superposition of atomic orbitals, which leads to an enhanced electron density () between the bonding nuclei. When electrons are placed into the bonding orbital, they spend most of their time between the nuclei of two atoms, which stabilizes the molecule.

1. What makes an antibonding orbital?

As shown in part A, the antibonding orbital results from the out-of-phase superposition of atomic orbitals, which leads to an attenuated electron density () between the bonding nuclei. When electrons are placed into the antibonding orbital, they spend less time between the nuclei of two atoms, which destabilizes the molecule.

4. According to the molecular orbital theory, the stability of a diatomic molecule can be characterized by the bond order that is based on the electronic configuration of the molecule. On the basis of the molecular orbital theory, explain why N2 is more stable than N2+, yet O2 is less stable than O2+.

The strength of bonding is characterized by the bond order, which is defined as

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where NA and NAB are the numbers of electrons in bonding orbitals and antibonding orbitals, respectively.

* 1. The electron configuration for the N2 molecule are (1s)2(\*1s)2(2s)2(\*2s)2

(2p)4 (2p)2, so the bond order of N2 is (10 − 4)/2 = 3.

The electron configuration for the N2+ ion are (1s)2(\*1s)2(2s)2(\*2s)2

(2p)4 (2p)1, so the bond order of N2+ is (9 − 4)/2 = 2.5.

Since N2 has a higher bond order than N2+, N2 is more stable than N2+.

* 1. The electron configuration for the O2 molecule is (1s)2(\*1s)2(2s)2(\*2s)2 (2p)2 (2p)4(\*2p)2, so the bond order of N2 is (10 − 6)/2 = 2.

The electron configuration for the O2+ ion is (1s)2(\*1s)2(2s)2(\*2s)2 (2p)2 (2p)4(\*2p)1, so the bond order of N2+ is (10 − 5)/2 = 2.5.

Since O2+ has a higher bond order than that of O2, O2+ is more stable than O2.