Hamiltonians

I. Atomic Hamiltonians

1. Basic coulomb Hamiltonian assuming an infinitely massive nucleus

$$\hat{H} = \hat{T} + \hat{V}$$

where

$$\hat{T} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2$$

is the electron kinetic energy operator for N electrons in atomic units. The potential energy operator has two parts

$$\hat{V} = \hat{V}_{en} + \hat{V}_{ee}$$

where, in atomic units, they are the electron-nucleus (atomic number Z) attraction operator

$$\hat{V}_{en} = -Z \sum_{i=1}^{N} \frac{1}{r_i}$$

and the electron-electron repulsion operator.

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{\left| \vec{r}_i - \vec{r}_j \right|} = \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

The kinetic energy operator and the electron-nucleus attraction operators both depend on a sum of terms, each of which depends on the coordinates of one electron, and consequently are often called one-electron operators and written as

$$\hat{F} = \hat{T} + \hat{V}_{en} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - Z \sum_{i=1}^{N} \frac{1}{r_i} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) = \sum_{i=1}^{N} \hat{f}_i$$

where

$$\hat{f}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$$

The electron-electron repulsion operator is a sum of terms, each of which depends on the coordinates of two electrons and is consequently called a two-electron operator and is often written as

$$\hat{G} = \hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} = \sum_{i<j}^{N} \frac{1}{r_{ij}} = \sum_{i<j}^{N} g(i,j)$$

where

$$g(i,j) = \frac{1}{r_{ij}}$$

The Hamiltonian then takes the very general form

$$\hat{H} = \sum_{i=1}^{N} \hat{f}_i + \sum_{i<j}^{N} g(i,j)$$

2. Spin-Orbit effects

3. External Fields

4. Relativistic

II .Molecular Hamiltonians

1. Basic Coulomb Hamiltonian in Born-Oppenheimer Approximation

$$\hat{H} = \hat{T} + \hat{V}$$

Where the kinetic energy operator for the N electrons is the same as the atomic case

$$\hat{T} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2$$

The Potential energy operator $\hat{V}$ consists of three terms: the electron-nuclear attraction, the electron-electron repulsion and the nuclear-nuclear repulsion

$$\hat{V} = \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

The electron-electron repulsion, V_{ee}, is the same as in the atomic case

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} = \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

while the electron-nuclear attraction, $\hat{V}_{en}$ is generalized to more than one nucleus

$$\hat{V}_{en} = -\sum_{k=1}^{nuclei} Z_k \sum_{i=1}^{N} \frac{1}{\left|\vec{r}_i - \vec{R}_k\right|} = -\sum_{k=1}^{nuclei} Z_k \sum_{i=1}^{N} \frac{1}{r_{ik}}$$

The nuclear repulsion term $\hat{V}_{nn}$ is given by

$$\hat{V}_{nn} = \sum_{k<l}^{nuclei} \frac{Z_k Z_l}{\left|\vec{R}_k - \vec{R}_l\right|} = \sum_{k<l}^{nuclei} \frac{Z_k Z_l}{R_{kl}}$$

and since the nuclei are fixed in the Born Oppenheimer approximation this term is a constant for a given nuclear configuration. As with the atomic case we may collect the components of the Hamiltonian into one and two electron operators

$$\hat{H} = \sum_{i=1}^{N} \hat{f}_i + \sum_{i<j}^{N} g(i,j) + \hat{V}_{nn}$$

Where

$$\hat{f}_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{nuclei} \frac{Z_k}{r_{ik}}$$

and

$$g(i,j) = \frac{1}{r_{ij}}$$

as in the atomic case. Often one defines an electronic hamiltonian by dropping $\hat{V}_{nn}$ and adding it to the final electronic energy to get the molecular energy. The electronic Hamiltonian has the form

$$\hat{H}_e = \sum_{i=1}^{N} \hat{f}_i + \sum_{i<j}^{N} g(i,j)$$

2. Spin-Orbit effects

3. External Fields

4. Relativistic

J. F. Harrison, September 2003