

Correlation Energy

It's informative to compare these Hartree results to experiment and the exact solution to the Schrodinger equation. The exact solution is from Pekeris who used a variational method based on the work of Hylleraas, *vide infra*.

atom	E(experiment) au	E(Schrodinger)**au	E(Hartree)*au	(E(S)-E(H)) eV
He	-2.903353	-2.903724	-2.861680	-1.144
Li ⁺	-7.279754	-7.279913	-7.236415	-1.184
Be ⁺²	-13.656441	-13.655566	-13.611299	-1.205
B ⁺³	-22.034560	-22.030972	-21.986234	-1.217
C ⁺⁴	-32.41562	-32.406247	-32.361193	-1.226
N ⁺⁵	-44.80104	-44.781445	-44.736164	-1.232
O ⁺⁶	-59.193482	-59.156595	-59.111143	-1.237
F ⁺⁷	-75.593926	-75.531712	-75.486126	-1.240
Ne ⁺⁸	-94.005023	-93.906807	-93.861113	-1.243

** Exact solution to the Schrodinger equation from Pekeris Physical Review 112, 1649 (1958)

..*Exact Hartree Energy from E. R. Davidson, *et. al*, Physical Review A. 44,7071, 1991

The first thing we note is that the exact solution differs from the experimental energy. This is due to several factors, the most important being relativistic corrections and the assumption that the nucleus is infinitely massive. The second observation is that the energy difference between the exact solution to the Schrodinger equation and the Hartree result is remarkably constant. The reason why the Hartree method cannot reproduce the exact solution is due to the inability of the Hartree wave-function to account for electron correlation. We know that the two electrons in He repel one another and absent any other factor they would stay as far apart as possible so that the probability of finding them close to one another would be small. Given the wave-function ψ the probability of finding electron 1 at the terminus of \vec{r}_1 and in the volume element dV_1 while electron 2 is at \vec{r}_2 in the volume element dV_2 is $\psi^2(\vec{r}_1, \vec{r}_2)dV_1dV_2$ which for the Hartree function is $\phi^2(\vec{r}_1)\phi^2(\vec{r}_2)dV_1dV_2$ and the probability is uncorrelated in that the location of electron 1 is independent of the location of electron 2. Another way of looking at this is to realize that the wave-function for the ground (spherically symmetric) state is a function of three variables: r_1 & r_2 the distances of the two electrons from the nucleus and r_{12} the distance between the electrons and the Hartree or orbital model doesn't include r_{12} in the trial function.