USE OF RELATIVISTIC EFFECTIVE CORE POTENTIAL IN THE CALCULATION OF ELECTRON-IMPACT TOTAL IONIZATION CROSS SECTIONS

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Based on the Binary-Encounter-Bethe (BEB) model, the advantage of using relativistic effective core potentials (RECP) in the calculation of total ionization cross sections of heavy atoms or molecules containing heavy atoms is discussed. Numerical examples for Ar, Kr, Xe, and WF_6 are presented.

The BEB model has been applied to a large number of atoms and molecules with good success.[1] Part of its attractiveness derives from the simple analytic expression for the cross section. For a bound electron in molecular orbital i, its BEB cross section is given by

$$\sigma_i = \frac{S_i}{t+u_i+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right]. \quad (1)$$

where $t = T/B_i$, $u_i = U_i/B_i$, and $S_i = 4\pi a_o^2 N_i (R/B_i)^2$, with T=incident electron kinetic energy, B_i= orbital binding energy, U_i= orbital kinetic energy, N_i = electron occupation number of the orbital, and R = Rydberg energy.

For heavy atoms, an electron with principle number $n \geq 3$ has most of its charge distribution outside the core region. Although the probability of its penetrating inside the core is small, once inside it moves with high velocity. On the other hand, ionization is much more likely to occur when the electron is outside the core and moving more slowly. For this reason, the orbital kinetic energy of high n electrons determined using standard wave function technique is unsuited for BEB calculations. Kim and coworkers[2] found that dividing $u_i + 1$ by the principle quantum number n of the high n electrons improves the BEB result significantly. This procedure approximately accounts for the fact that (1) most of the electron charge distribution is outside the core region, and (2) the average kinetic energy outside the core region is much lower.

An alternate approach is to employ an effective core potential (ECP) in the wave function calculation. Here the core electrons are replaced by an ECP which allows much less penetration by the outer electron. Indeed, the orbital kinetic energies of the outer electrons are significantly decreased when an ECP is used. For Ar, the kinetic energy of the 3s and 3p electrons from a Dirac-Fock (DF) calculation are 3.8385 and 2.8963 harrtree, respectively, while the RECP Hartree-Fock calculation gives 0.6861 and 1.8501 hartree. Note the large decrease of the kinetic energy from the RECP calculation, and the reverse ordering of 3s and 3p kinetic energies.

Figure 1 presents the BEB cross sections of Ar determined using all electron DF calculation with n scaling as well as the cross sections using RECP Complete-Active-Space (CAS) SCF calculations with no scaling. Also presented are the experimental data by Rapp and Englander-Golden[3] and by Straub et al.[4] The all electron calculation with n scaling agree better with experiment at low T, and the RECP-CASSCF calculation agree better with experiment near the peak of the cross section curve.

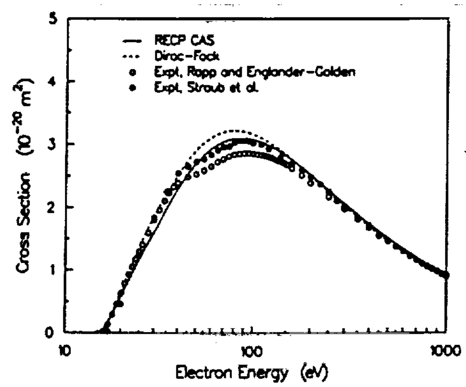

Figure 1. Total ionization cross section of Ar

Calculations of BEB cross sections for Kr, Xe, and WF_6 will be presented at the conference.

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