TWO ELECTRON PROBLEM - MONTE CARLO METHOD

S. Basu
Dept. of Chemistry, University of Colombo

Despite the widespread prevalence of computing facilities in universities, students of the physical sciences remain generally unfamiliar with the use of computers in practice. For example, it is found frequently that while quantum mechanics and other theoretical course refer to the use of Monte Carlo methods for the solution of numerical problems, their significance is rarely grasped by the student. In this paper, we illustrate a simple application of this numerical technique to optimise the exponential parameters (α and β) of hydrogenic is basis functions for the 2 electron atom (nuclear charge +Ze) problem. A simple analytical solution is possible only in the case of equal exponents ($\alpha = \beta$). For $\alpha \neq \beta$, this routine has been tested with Z = 1 to 4 using single and double precision on a 16-bit microcomputer. It is found that the search converges rapidly to a minimum of energy and to stable values of α & β (to 4 significant figures) with the search restricted to $\pm$5% of the trial values in a particular iteration. It can be seen that the optimised energies for $\alpha \neq \beta$ are considerably lower than those from the simple variation method in which the exponents are constrained to be equal. In fact, they compare favourably with Hartree-Fock energies, eg. the HF energy for the ground state of the He atom is -2.8617 au - above the -2.8757 au minimum found for this trial function. In the case of H^-, this trial function correctly predicts a bound state unlike the simple variation method. For He, the correlation energy (the difference between the calculated energy and the "exact" value) has been brought down to 0.0281 au compared with 0.0421 au for the Hartree-Fock method and 0.0247 au for the 'S' limit (ie. using the complete set of s basis functions in the trial function). The trial function used in this paper yields over 80% of the radial correlation energy. Similarly for other 2-electron species, this trial function lowers the energy with $\alpha > Z$ and $\beta < Z$. Such ('open-shell') functions ($\alpha \neq \beta$) describe the electron experiencing different levels of screening from the nucleus.

A simple implementation, in BASIC, is presented of optimisation by random sampling as an alternative to the analytical approach (applied in few cases) or to optimisation by least means square methods. The Monte Carlo method, in this case, is generally less efficient but it does allow the physics to be clearly discernible. This simple optimisation method allows the solution of a non-trivial problem using BASIC on desktop microcomputer.