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LETTER TO THE EDITORS

Some Comments on Cini's "Ionization Potentials and Electron Affinities of Metal Clusters"

In a recent communication, Cini (*1*) has suggested that unjustified assumptions were made regarding the application of molecular orbital theory to the calculation of ionization potentials (IP) and electron affinity (EA) of metal clusters (*2, 3*). The grounds for the criticism are that extended Hückel theory (EH) gives EA values for the cluster larger than those of the bulk metal. While agreeing that the EH results calculated as before are undoubtedly larger than experimental values, I believe the criticisms of the application of molecular orbital theory are unjustified and fail to account for recent calculations on Ag clusters (*4*) giving more accurate EA values. I wish to address these points and comment on the Jellium model.

Semi-empirical molecular orbital theories including EH and CNDO are approximate and while some quantities can be calculated more accurately than others, no claims of absolute agreement with experiment have been made as indicated in the conclusions of Ref. (*2*). These theories are used to predict trends with size of the metal cluster. The assignment of IP with the highest occupied molecular orbital and EA with the lowest unoccupied molecular orbital represent a widely used first approximation when using EH because these are the molecular orbitals to which electrons are added or removed in the respective processes. Consider the values of IP and EA for Ag and other metal clusters resulting from this assignment (*2, 3*). They show convergence with increasing size as expected from physical models. Some irregularities in the trend dependent upon geometry were found. The values settle near 5.5 eV for the largest three-dimensional Ag clusters which admittedly is larger than the bulk work function (4.3 eV), but hardly a large error.

The absence of explicit electron repulsive effects in the model accounts for the large EA values calculated by EH. These effects are treated by CNDO and reflected in the data of Table V of Ref. (*4*) for isolated Ag clusters which Cini ignores in his criticisms. The EA values calculated by CNDO are lower than the values calculated by EH and much less than the work function of bulk Ag. These data show that the effect of electrostatic forces on EA values can be determined by electron energy levels in molecular orbital theory.

Values of IP calculated by EH from the highest occupied molecular orbital follow trends of experimental data within a series of similar molecules or clusters. For molecules such as the alkanes, calculated values are about 2 eV larger than experimental (*5*). In the case of Na clusters of small size, calculated IP values are about 1 eV larger than experimental values (*6*). These data show that the identification of the highest occupied molecular orbital with IP within the framework of molecular orbital theory is justified. The well-known Koopmans' theorem is the basis of this procedure.

Let us turn to the results of Cini and the Jellium model. The model gives IP values matching Na experimental values and at small *R* the IP agrees with the value for the Na atom. In the case of Ag, the experimental atom IP is almost 2.5 eV larger than Na, yet the calculated curves of Cini's Fig. 1 and 2 show a remarkable insensitivity to this effect. They also do not extrapolate to the IP of the Ag atom at small *R* which is 7.56 eV. On the other hand, IP values calculated by EH are closer to this value and the IP of Ag_2 calculated by CNDO is 7.23 eV (*2*). It would also be interesting to compare other quantities such as binding energies of the small clusters.

The Jellium model employed in Cini's paper was based on derivations by Hohenberg and Kohn (*7*) (HK) for a system with uniform background of positive charge where the electron density is a slowly varying function. This model works well for bulk and the surface of free electron metals treating the sea of free electrons interacting with an average positive background. In the case of small metal clusters, there are only a few valence electrons interacting with the point nuclear charges. The Jellium model of uniform positive background density seems much less realistic here. Despite this, each type of model calculation has its strengths and weaknesses and they should be interpreted accordingly.

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