JOURNAL OF CATALYSIS **47**, 140–143 (1977)

# NOTES

## Comments on the Crystal Field Surface Orbital–Bond Energy Bond Order (CFSO BEBO) Approach

The CFSO BEBO approach, introduced to surface science and catalysis by Weinberg *et al.* (*1–6*), seems to represent a quantitative semiempirical exploitation of the qualitative "chemical" description of surface processes in terms of localized surface orbitals. Working with a minimum of mathematical apparatus, it enables one to obtain the potential energy versus reaction coordinate (or the bond order) curves, and thereby the activation energies and reaction heats. Some very optimistic judgments of the CFSO BEBO method have appeared (*7–10*) and in some cases the bond energy values obtained by this method have been referred to as well-established values (*11*). It seems therefore useful to summarize and to comment on the assumptions and limits of the CFSO BEBO approach.

The CFSO BEBO method starts with energy balance considerations, where the dependence of the individual energy terms on distances between particles (or the reaction coordinate) follows from the BEBO correlations in the gas molecules. In chemisorption various chemical bonds are dissociated and newly formed. However, the relevant BEBO correlations are available for a limited number of bonds only. The interrelation of all bond orders involved in the investigated process has therefore to be found. The final equation of the potential energy curve for a given surface process then usually rests upon only a single BEBO correlation.

The application of the BEBO approach (*12*) in the field of surface interactions is based on the following assumptions.

i. *Partially occupied orbitals, localized on individual atoms, occur on solid surfaces, including metals.*

The occurrence of such orbitals on transition metal surfaces [for which the CFSO BEBO method has been exclusively used (*1–6*)] cannot be substantiated from the crystal field theory [see, e.g., (*3*)], as originally suggested (*1–6*). It thus seems reasonable to omit "crystal field" from the name of this approach. However, some experimental indications for the validity of this assumption can be found (*14–17*), *viz,* that the surface atoms in the very moment of the interaction with the approaching gas particle can be represented by spatially directed localized orbitals (*5, 18, 19*).

ii. *The occupation of the localized surface orbitals by electrons is postulated.*

The physical basis for the fractional occupation numbers of localized surface orbitals is far from being obvious, and reliable data for this quantity even for the bulk atoms are lacking, particularly for high electron density metals [see, e.g., (*20*)]. The partially occupied localized surface orbitals are needed in the CFSO BEBO approach for the description of the first step of adsorption (see, e.g., $H_2$–$Pt_2$ interaction (*3*), mentioned in Sect. (v) of this note].

ISSN 0021-9517

iii. *The BEBO correlation for a particular bond, estimated in a gas molecule, holds exactly for that molecule in the adsorbed state.*

Because of a complete lack of relevant experimental data, it is difficult to judge the validity of this assumption. However, it is known from the literature [e.g., Refs. (*21*, *22*)] for analogous systems that the equilibrium geometry of an isolated molecule may undergo substantial distortion when exposed to the field of a complex metal ion. Moreover, the experimental basis for the BEBO correlation even for the gas molecule is sometimes not a very reliable one: for example, the BEBO correlation for the gaseous hydrogen molecule (which often plays an important role in various surface processes) is based on three experimental points only, namely, the hydrogen molecule in the ground and excited states (bond lengths $0.8 \times 10^{-10}$ and $1.0 \times 10^{-10}$ m) and the He–He molecule (bond length $2.9 \times 10^{-10}$ m) (*3*, *12*).

iv. *One particular bond splitting and another bond formation is investigated by the BEBO method for an a priori postulated geometrical configuration of the system,* resulting neither from the CFSO BEBO procedure itself, nor from the experiment.

The choice of a particular system configuration is speculative unless we take into account many alternatives of the mutual geometrical arrangement of the approaching gas molecule and the surface atoms, giving the best value of one (or better more than one) observable quantity, e.g., adsorption heat. This purely empirical optimization procedure has not been performed yet.

It is assumed, e.g., for the $H_2$–$Pt_2$ interaction, that the two hydrogen atoms of the hydrogen molecule, adsorbing on the platinum (111) plane (represented by two platinum atoms only), are approaching the surface in the plane of platinum $t_{2g}$ orbitals (*3*). The equilibrium position of the hydrogen atoms with respect to the two platinum atoms is postulated and the computation is stopped there. Then the result can be fitted to the experimental value of the adsorption heat, for example, by appropriate choice of the platinum–hydrogen single bond energy.

v. *The mechanism of the particular surface process* (the sequence of the reaction steps in which some bonds are split and others newly formed) *is postulated* and does not result from the CFSO BEBO computation.

The mathematical relations among the bond orders in the gas molecule, in the surface and in the chemisorption complex (necessary for the evaluation of the potential energy curves) can be formulated only after the mechanism of the process and the geometrical arrangement of the reactants have been postulated. Since no optimization procedure (analogous to the one suggested in the preceding section) has been performed yet, the results of the CFSO BEBO computation can be fitted to the values of experimental quantities by appropriate choice of the reaction mechanism, thus losing predictive power.

The arbitrariness of this procedure can be seen, for instance, in the case of hydrogen adsorption on platinum (*3*). It is first assumed that the hydrogen molecule is adsorbed without changing the bond order of the $Pt_2$ cluster, using partially occupied surface orbitals only. Then the hydrogen molecule is dissociated. During this step the Pt–H bond energy (bond order) increases with no change of Pt–H distance, at variance with the general BEBO principles. Finally the hydrogen atoms move to a priori postulated equilibrium positions, with additional increase of the Pt–H bond energy (bond order). The Pt–H distance in this last step increases, in contrast to the BEBO expectation. Intuitively one could understand this paradox in terms of multiple bond formation with further platinum atoms. However, no additional platinum atoms were taken into account in the numerical calculation (*3*). The CFSO

BEBO procedure is thus in this particular case invalidated by internal inconsistency.

vi. *Reliable values for single bond energies are mostly unknown and it is supposed that the simplified Pauling "mixing rules" (3) can be used for obtaining them.*

In some cases the single bond energy is claimed to be the only adjustable parameter of the CFSO BEBO approach (*6*) (see the preceding section). This statement is questionable, as can be seen in the case of the Pt–Pt single bond, for which the value $E_{\mathrm{Pt-Pt,\ single}} = 43.6$ kcal/mole has been chosen (*1–6*) in contrast to 20–22 kcal/mole generally used in the literature (*23, 24*). Consequently, the agreement concerning the value $E_{\mathrm{Pt-H,\ single}} = 67$ kcal/mole, obtained both in (*3*) and (*24*), is meaningless, due to the following reasons. This value has been obtained in (*3*) as a geometric average of $E_{\mathrm{H-H,\ single}} = 103.2$ kcal/mole and $E_{\mathrm{Pt-Pt,\ single}} = 43.6$ kcal/mole. In (*24*) it has been obtained as an arithmetic average of the same $E_{\mathrm{H-H,single}}$ and $E_{\mathrm{Pt-Pt,\ single}} = 20.7$ kcal/mole, taking into account the empirical correction for Pt–H dipole moment. Thus the different forms of the same Pauling "mixing rule" (*25*) have been used with different values for $E_{\mathrm{Pt-Pt,\ single}}$ (and different corrections). Similarly the procedure of obtaining the value $E_{\mathrm{Pt-C,\ single}} = 62.5$ kcal/mole by arbitrary combination of geometric and arithmetic averages, as described in (*6*), is hardly justifiable.

In conclusion it should be mentioned that the CFSO BEBO potential curves have unrealistic shapes, since they do not take into account repulsive interactions (with the exception of that part of the potential energy curve representing physical adsorption (*3*), where the ordinary Lennard-Jones potential has been used, having no relation to the CFSO BEBO procedure itself). In this connection one should compare the potential energy curves of Fig. 8 in (*3*) and Fig. 2 in (*5*) with each other and both of them with the generally accepted type of potential energy curves for adsorption [see, e.g., Fig. 4.10, p. 68 in (*26*)]. The CFSO BEBO equations represent monotonic functions, exhibiting no extremes. The complete potential energy curve is constructed with respect to the postulated reaction mechanism and the system configuration by *discontinuous combination of intervals* (postulated reaction steps) *with monotonically increasing or decreasing functions* (polynoms, constructed from BEBO correlations), *which intersect at the interval boundaries.* These intersections are considered in the CFSO BEBO formalism to be "maxima" (related to the activation energies) and "minima" (related to the reaction heats) and their coordinates directly follow from the postulated system configurations during the individual reaction steps. The absolute values of both activation energies and reaction heats (heats of adsorption) are thus uncertain (*3, 6*). The CFSO BEBO approach contains a considerable number of assumptions, which until now are mostly of a speculative character, giving a wide variety of possibilities for successful fitting of the formal description to some experimental data. Its predictive power is thus very limited.

Empirical or semiempirical approaches are useful, when they help to find some as yet unknown relations among the experimental data, or if the empirically found relations can substantially lower the number of measurements necessary for the exact description of a given process. As shown in this note, the CFSO BEBO approach does not meet these requirements. Therefore it seems reasonable to concentrate efforts on the more sophisticated theories, though they are based on simplified models, too (*27–32*). In the field of surface chemical interactions it seems promising to include into the models of transition metal surfaces used in the theoretical considerations both the partially localized $d$-electrons and the high density of the nearly free electrons (*33–36*).

## ACKNOWLEDGMENTS

I am grateful to S. Černý and J. Müller for a critical reading of the manuscript.

## REFERENCES

*1.* Weinberg, W. H., *J. Catal.* **28**, 459 (1973).
*2.* Weinberg, W. H., Lambert, R. M., Comrie, C. M., and Linnett, J. W., *Surface Sci.* **30**, 299 (1972).
*3.* Weinberg, W. H., and Merrill, R. P., *Surface Sci.* **33**, 493 (1972).
*4.* Weinberg, W. H., and Merrill, R. P., *Surface Sci.* **39**, 206 (1973).
*5.* Weinberg, W. H., *J. Vac. Sci. Technol.* **10**, 89 1973).
*6.* Weinberg, W. H., Deans, H. A., and Merrill, R. P., *Surface Sci.* **41**, 312 (1974).
*7.* Yates, J. T., *Chem. Eng. News*, Aug., 19 (1974).
*8.* Hobson, J. P., *in* "Advances in Colloid and Interface Science," Vol. 4, p. 79. Elsevier, Amsterdam, 1974.
*9.* Baetzold, R. C., *Surface Sci.* **51**, 1 (1975).
*10.* Tompkins, F. C., *in* "Critical Reviews in Solid State Sciences," (F. D. Schuele, and R. W. Hoffman, Eds.), Vol. 4, p. 279. Elsevier, Amsterdam, 1974.
*11.* Baron, K., Blakely, D. W., and Somorjai, G. A., *Surface Sci.* **41**, 45 (1974).
*12.* Johnston, H. S., "Gas Phase Reaction Rate Theory," Ronald Press, New York, 1966.
*13.* Brooks, H., *in* "Electronic Structure and Alloy Chemistry of Transition Metals" (P. A. Beck, Ed.). Wiley, New York, 1963.
*14.* Knor, Z., and Müller, E. W., *Surface Sci.* **10**, 21 (1968).
*15.* Madey, T. E., Czyzewski, J. J., and Yates, J. T., *Surface Sci.* **49**, 465 (1975).
*16.* Feuerbacher, B., *Surface Sci.* **47**, 115 (1975).
*17.* Waclawski, J., Vorburger, T. V., and Stein, R. J., *J. Vac. Sci. Technol.* **12**, 301 (1975).
*18.* Knor, Z., *J. Vac. Sci. Technol.* **8**, 57 (1971), *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 51. Academic Press, New York, 1972.
*19.* Kölbel, H., and Tillmetz, K. D., *J. Catal.* **34**, 307 (1974).
*20.* "Phase Stability in Metals and Alloys" (P. Rudman, J. Stringer and R. I. Joffee, Eds.). McGraw-Hill, New York, 1967.
*21.* Hewitt, T. G., and De Boer, J. J., *J. Chem. Soc. A* 817 (1971).
*22.* Řeřicha, R., and Hetflejš, J., *Collect. Czech. Chem. Commun.* **40**, 1811 (1975).
*23.* Ehrlich, G., *J. Chem. Phys.* **31**, 1111 (1959).
*24.* Higuchi, I., Ree, T., and Eyring, H., *J. Amer. Chem. Soc.* **79**, 1330 (1957).
*25.* Pauling, L., "The Nature of the Chemical Bond." Cornell University Press, Ithaca, 1960.
*26.* Clark, A., "The Chemisorption Bond." Academic Press, New York, 1974.
*27.* Schrieffer, I. R., *J. Vac. Sci. Technol.* **13**, 335 (1976).
*28.* Johnson, K. H., and Messmer, R. P., *J. Vac. Sci. Technol.* **11**, 236 (1974).
*29.* Baetzold, R. C., *Surface Sci.* **51**, 1 (1975).
*30.* Fassaert, D. J. M., and Van der Avoird, A., *Surface Sci.* **55**, 291 (1976).
*31.* Gadzuk, J. W., *Surface Sci.* **43**, 44 (1974).
*32.* Grimley, T. B., *in* "Structure and Properties of Metal Surfaces," p. 72. Maruzen, Tokyo, 1973.
*33.* Tsang, Y. W., and Falicov, L. M., *J. Phys.* **C9**, 51 (1976).
*34.* Madhukar, A., and Bell, B., *Phys. Rev. Lett.* **34**, 1631 (1975).
*35.* Bell, B., and Madhukar, A., *J. Vac. Sci. Technol.* **13**, 345 (1976).
*36.* Knor, Z., *in* "Surface and Defect Properties of Solids," Specialist Periodical Reports (M. W. Roberts and J. M. Thomas, Eds.). Chem. Soc. London, in press.

Z. Knor

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry*
*Czechoslovak Academy of Sciences*
*121 38 Prague 2, Czechoslovakia*

*Received March 24, 1976; revised December 6, 1976*