On the future of the Hückel model

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Abstract

In an attempt to foresee the prospects of the qualitative trend in quantum chemistry, the place of the Hückel model is analyzed in the broad context of quantum mechanical and chemical perspectives on the molecular world. Quantum mechanics and chemistry are considered as complementary approaches to molecular structure and properties that are irreducible one to another. Arguments are given for the hypothesis that the Hückel model makes a separate level of investigation of molecules situated in between quantum mechanics and chemistry. In this context, the need is emphasized for development of new concepts immanent in the very Hückel model. These concepts are anticipated to play the role of terms for qualitative orbital thinking, the persistent need for which was emphasized recently (R. Hoffmann, J. Mol. Struct. (Theochem), 424 (1998) 1). © 1999 Elsevier Science B.V. All rights reserved.

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The relation between computation and understanding in quantum chemistry has been discussed recently in Refs. [1,2]. As was emphasized by Hoffmann, understanding the molecular structure and properties lags behind their predictability following from the contemporary calculations of electronic structures. It was claimed in this connection that a persistent need for qualitative orbital thinking arises nowadays.

Qualitative thinking in terms of orbitals implies taking into account the principal interactions between basis orbitals (e.g. AOs) of the given molecule and imagining the shapes of the final molecular orbitals and their relative positions in the energy scale. Mental reasoning or simple algebra (but not self-consistent calculations) are appropriate approaches here. It is also essential that "weights" of particular basis functions (AOs) within molecular orbitals are sought, and not quite exact shapes of the very basis functions are

required for such purposes. The above mentioned process is likely to be nothing more than an application of the Hückel model.

We should come to an agreement here about the meaning of the concept "the Hückel model". Thus, the original version of the model [3,4] was intended to be the first semiempirical method of calculation of electronic structures of polyatomic molecules. Numerical values of the principal parameters (α and β) should be necessarily specified in this case. In the above-cited papers these parameters were determined on the basis of the best coincidence of results of calculation of a few reference compounds with the relevant experimental data. Understanding of the Hückel model as an extremely approximate method of calculation of electronic structures is a widespread viewpoint up to now. When accepting this point of view, however, the qualitative aspects of the model become ignored. However, just these aspects of the Hückel model form the basis of qualitative orbital thinking.

The qualitative content of the Hückel model has

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little to do with the numerical values of its parameters. The main point here consists in the fact that the structure of a model Hamiltonian matrix reflects the spatial and/or chemical constitution of the respective molecule.

Indeed, certain basis orbitals (AOs) are assumed to correspond to diagonal elements (α) of the Hückel type Hamiltonian matrices ($\mathbf{H}$), whilst the off-diagonal elements (β) represent the interactions between these orbitals. The latter, in turn, are usually assumed to be proportional to overlap integrals [5] being directly dependent on both the respective internuclear distance and the spatial arrangement of basis orbitals. As a result, the above mentioned interrelation between the structure of the matrix $\mathbf{H}$ and that of the given molecule arises. For conjugated hydrocarbons, this relation is known to acquire an extremely simple form, namely, the model Hamiltonian matrix $\mathbf{H}$ in the basis of $2p_z$ AOs of carbon atoms proves to be proportional to the adjacency matrix of the graph describing the structure of the C-skeleton of the given molecule [6]. In the case of saturated hydrocarbons, a somewhat more involved relation has been established between the matrix $\mathbf{H}$ and the adjacency matrix of the chemical graph [7,8].

Thus, let the concept "the Hückel model" embrace both the qualitative and the quantitative aspects of the approach. It is evident that if we take a simple matrix $\mathbf{H}$ and diagonalize it in a mental way, we are actually in a process of the qualitative orbital thinking. Alternatively, if we construct an involved model Hamiltonian matrix containing several types of parameters and diagonalize it algebraically, e.g. by means of the perturbation theory, we obtain a qualitative method of investigation of polyatomic molecules (see e.g. [9–11]). It is essential here that neither the basis orbitals nor the one-electron Hamiltonian operator underlying the matrix $\mathbf{H}$ are defined explicitly. Moreover, in practice, necessity for such a definition does not arise. This aspect makes the Hückel model and the qualitative orbital thinking even closer.

Hence, we arrive at a conclusion that the qualitative orbital thinking is a particular way of application of the Hückel model. This implies that the prospects of the former actually depend on further advances in the field of the latter. In this context, understanding of the nature of the Hückel model is of great importance for further development of the qualitative orbital thinking.

The Hückel model is commonly considered only as a rough approximation to the Hartree–Fock–Roothaan equation. This point of view is in line with the above mentioned meaning of the Hückel model as an approximate quantum chemical method of calculation of electronic structures. However, there are reasons to believe that this standpoint is a great oversimplification of things. To demonstrate this, we are about to discuss in this article the place of the Hückel model in a much broader context as compared to the traditional one, namely in the context of perspectives of quantum mechanics and of the classical chemistry on the molecular world. To this end let us consider these perspectives separately at first.

Let us start with the quantum-mechanical perspective. Molecules are considered as systems of interacting elementary particles, viz. of electrons and of nuclei, in this scientific field. Although a single fundamental equation, namely the Schrödinger's equation, describes the whole diversity of molecules, only its particular cases corresponding to specific values of the principal parameters may be actually solved (just the numbers of electrons and nuclei play the role of these parameters).

Each molecule is evidently described by its own number of electrons and nuclei. As a result, each individual representative of the molecular world is studied separately in the framework of the quantum theory. Thus, no immanent relation may be established between the Schrödinger's equations for two molecules even if their chemical structures are very similar (e.g. for methane and ethane), and these problems are entirely independent. This implies that similarity of molecules may be revealed only after comparison of the final solutions of the Schrödinger's equations. Such a resemblance of solutions (if any) may be called an a posteriori similarity.

Therefore, studies of individual representatives of the molecular world and a posteriori similarities of electronic structures of definite groups of compounds are the main features of the quantum mechanical perspective on molecules.

Alternatively, it is the whole of molecules that is the main subject of chemistry. The principal approach of this scientific field consists in distinguishing separate series and classes of the so-called related compounds, i.e. in classification of molecules. Moreover, along with rules governing the observed

properties inherent in their series, common properties of molecules belonging to the same class are among the problems of chemical interest. It is noteworthy that classification is among the principal approaches also of other natural sciences (e.g. of biology) but not of physics.

Moreover, similarity of chemical constitution of certain group of molecules is assumed a priori in this case. In other words, common structures is an assumption, whilst common properties is an anticipation in chemistry. Moreover, it is the a priori similarity that forms the basis of the chemical classification of molecules. For example, alkanes are distinguished as a separate class of chemical compounds just owing to an a priori similarity of their structures. It should be emphasized here that the chemical constitution of molecules that forms the basis of the above discussed classification is defined in terms of atoms involved within the given compound and the way these are bound together. This definition has nothing to do with the numbers of electrons and of the nuclei.

On the whole, atoms in molecules and chemical bonds are the principal terms of the classical chemistry. It is noteworthy that the exact meaning of these terms are not essential in practice. It is no surprise, therefore, that the chemical way of description of the molecular world in terms of chemical formulas was used long before the emergence of quantum mechanics that gave an explanation of the nature of chemical bond in the simplest molecules [12]. Nowadays this way of description also exits almost independently of the quantum mechanical analogues of the chemical bonds being permanently sought by quantum chemists. To make sure that this is the case, it is no more required to take a common chemistry textbook.

It is quite likely in this connection that the meaning of certain chemical formula can be defined only in the context of other chemical formulas. For example, the formula CH_3-OH primarily implies the similarity of the definite part of this molecule, viz. of the CH_3- group, to respective part of a saturated hydrocarbon (e.g. CH_3-CH_3), whilst the remaining fragment (OH) resembles that of the water molecule (H–OH). The concept of molecular fragments (functional groups) naturally arises in this context.

Therefore, description of the whole molecular world in terms of chemical formulas reflecting the a priori similarity of particular groups of compounds, viz. of series and classes of molecules, forms the basis of the classical chemical perspective.

If we compare this standpoint to the quantum mechanical one, the chemical perspective consists in looking at the whole molecular world from above (and we have to ascend as high as to be able to see the whole variety of molecules), whereas the quantum mechanical perspective corresponds to looking at the same world from below. It is evident that these two standpoints are irreducible one to another and may be considered as complementary approaches.

Let us turn again to the Hückel model. There are good reasons to expect that the Hückel model takes an intermediate place between the above described two approaches. Let us discuss this point in a more detail.

It is evident that we cannot ignore the quantum mechanical origin of the Hückel model. Indeed, both the model itself and its results are formulated in terms of quantum mechanics, e.g. one-electron orbitals, one-electron energies, etc. The fact that the Hückel type Hamiltonian matrix may be considered as a rough approximation to the respective matrix of the self-consistent Fockian also is beyond any doubt.

Nevertheless, there are some essential common features between the Hückel model and the chemical way of description molecules.

First, the role of the number of electrons in the formation of electronic structures is extremely reduced in the Hückel model. Indeed, molecular orbitals are being sought here without regard to the number of electrons.

Second, the meaning of the principal parameters of the model (α and β) is not defined explicitly as it is the case with atoms in molecules and chemical bonds.

Third, relations may be established between the Hückel type Hamiltonian matrices and the adjacency matrices of graphs describing the respective chemical formulas [6–8] as discussed earlier in this article.

Henceforth, the way the similarity of related molecules is described in the Hückel model resembles that of chemistry. Let us dwell on this important aspect in more detail.

Thus, similarity of constitution of the initial model Hamiltonian matrices of related molecules is assumed a priori within the Hückel model. For example, the α and β parameters of polyenes, polyacenes, etc. are commonly assumed to be uniform over the whole

chain and independent of the structure of the particular molecule [13]. The principal point, however, consists in the fact that assumptions of the above described type lead to non-trivial consequences.

Indeed, after accepting the above mentioned simplifications, a single Hückel type Hamiltonian matrix may be attributed to the whole series of related molecules (e.g. polyenes), wherein the number of similar fragments plays the role of the principal parameter. Accordingly, a single eigenvalue problem may be solved for this matrix, and the resulting solution depends on the number of similar fragments [13]. As a result, the whole series of related molecules gets described as a single object in the framework of the Hückel model. It is evident that this generalized description is something more than the sum of descriptions of particular representatives of the series.

Hydrocarbons and their derivatives is another example of similar molecules. The respective Hückel type Hamiltonian matrices differ only in the value of a single parameter, viz. of the Coulomb parameter (α) referring to the site of substitution (see e.g. [5]). As a result, the two secular problems may be considered as a single problem, wherein the α value plays the role of the principal parameter. Thus, the electronic structure of the substituted molecule becomes described in terms of that of the parent hydrocarbon. This way of investigation is evidently in line with the chemical concept of the derivative.

Finally, common Hückel type Hamiltonian matrices for entire classes of molecules, e.g. for alkanes, along with respective generalized problems (the so-called eigenblock equations) should be mentioned [14,15]. As with series of related compounds, the class under study also becomes described as a single object on the basis of the Hückel model.

Therefore, we have to assume in this situation that the Hückel model makes a separate level of investigation of molecules situated in between quantum mechanics and chemistry. This implies that the qualitative orbital thinking is irreducible either to quantum mechanical or to chemical ways of thinking. Analysis of passing from quantum mechanics to the Hückel model demonstrates to us how this irreducibility arises.

Thus, details of constitution of one-electron Hamiltonian matrices of particular molecules are ignored when turning from the Hartree–Fock–Roothaan equation to the Hückel model. For example, the Coulomb parameters α of ethylene evidently differ from those of butadiene, but these differences are neglected. On the contrary, it is the simplifications of the above mentioned type that make possible the common description of series of related molecules in the framework of the Hückel model. Hence, ignoring some details allows certain generalization to be made that is irreducible to the sum of its particular cases. In other words, a new level of investigation becomes possible at the expense of certain loss of accuracy when describing particular cases.

Irreducibility of the Hückel model either to quantum mechanics or to chemistry implies that explanation and/or interpretation of the results of the computational quantum chemistry is hardly the main aim of qualitative orbital thinking, and the latter has its own "raison d'être" and its own future.

As it was described earlier, both quantum mechanics and chemistry are based on their own systems of fundamental concepts. It was also demonstrated that the Hückel model has appropriated certain concepts of quantum mechanics and of chemistry. However, the future of the model is likely to depend on development of its own system of concepts that should play the role of terms for qualitative orbital thinking. A mental diagonalization of simple matrices is evidently not sufficient for this purpose, and more profound studies of possibilities of the model are required here.

History of the Hückel model shows that new concepts emerged in the process of its development. Thus, the original concept of the orbital–orbital polarizabilities was suggested when studying the heteroatom influence in conjugated hydrocarbons [16–19]. Moreover, the concept of the through-space and through-bond interactions has been proposed for interpretation of photoelectron spectra of molecules [20–22]. Later, these concepts have also been applied for interpretation of the structures of localized molecular orbitals and of the one-electron density matrices (bond order matrices) [15,23]. The concepts of the intramolecular charge transfer and intrabond polarization suggested recently [24] also seem to be fruitful.

So, let this history be continued…

References

[1] R. Hoffmann, J. Mol. Struct. (Theochem) 424 (1998) 1.

[2] J.-P. Malrieu, J. Mol. Struct. (Theochem) 424 (1998) 83.

[3] E. Hückel, Z. Phys. 70 (1931) 204.

[4] E. Hückel, Z. Phys. 76 (1932) 628.

[5] R. Zahradnik, R. Polák, Elements of Quantum Chemistry, Plenum Press, New York, 1980.

[6] N. Trinajstic, Topology and Hückel theory, in: G. Segal (Ed.), Semiempirical Methods of Electronic Structure Calculations, 1, Mir, Moscow, 1980, p. 46, in Russian.

[7] V. Gineityte, Int. J. Quant. Chem. 53 (1995) 245.

[8] V. Gineityte, Croatica Chem. Acta 71 (1998) 673.

[9] J. Pople, D.P. Santry, Mol. Phys. 71 (1963–64) 269.

[10] K. Konstantinavicius, J. Mol. Struct. (Theochem) 312 (1994) 145.

[11] K. Konstantinavicius, J. Mol. Struct. (Theochem) 392 (1997) 193.

[12] J.C. Slater, Electronic Structure of Molecules, McGraw-Hill, New York, 1963.

[13] S. Huzinaga, The MO Method, Mir, Moscow, 1983, in Russian.

[14] V. Gineityte, J. Mol. Struct. (Theochem) 333 (1995) 297.

[15] V. Gineityte, J. Mol. Struct. (Theochem) 343 (1995) 183.

[16] C.A. Coulson, H.C. Longuet-Higgins, Proc. R. Soc. A191 (1947) 39.

[17] C.A. Coulson, H.C. Longuet-Higgins, Proc. R. Soc. A192 (1947) 16.

[18] C.A. Coulson, H.C. Longuet-Higgins, Proc. R. Soc. A193 (1948) 447, see also p. 456.

[19] C.A. Coulson, H.C. Longuet-Higgins, Proc. R. Soc. A195 (1948) 188.

[20] R. Hoffmann, A. Imamura, W.J. Heere, J. Am. Chem. Soc. 90 (1968) 1499.

[21] E. Heilbronner, A. Schmelzer, Helvetica Chem. Acta 58 (1975) 936.

[22] R. Hoffmann, E. Heilbronner, R. Gleiter, J. Am. Chem. Soc. 92 (1970) 706.

[23] V. Gineityte, J. Mol. Struct. (Theochem) 430 (1998) 97.

[24] V. Gineityte, J. Mol. Struct. (Theochem) 434 (1998) 43.