

Electronic Chemical Potential and Orbital Electronegativity of Univalent Substituents

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Abstract—The relations were analyzed between the electronic chemical potential of a chemical group in the ground state and the orbital chemical potential of its valence state, the latter being equal in absolute value to its orbital electronegativity. These quantities should be equivalent for univalent substituents whose ground electronic state can be described by one-determinant wave function allowing localization of molecular orbitals in a closed shell. In this case, the orbital electronegativity of a chemical group can be calculated in terms of nonempirical quantum-chemical methods. The results of the variation calculation of orbital electronegativities of a series of univalent substituents gave rise to a quantum-chemical scale of group electronegativities which may be used for testing of approximate calculation procedures.

The electronic chemical potential (CP) of an atom, molecule, or radical species is defined by the following formal mathematical expression:

$$\mu = \left[\frac{\partial E}{\partial N} \right]_{v(\mathbf{r})}, \quad (1)$$

where N is the number of electrons, and $v(\mathbf{r})$ is the electrostatic potential of nuclei, which depends on the charges and geometric configuration of the stationary nuclear subsystem [1]. The quantities N and $v(\mathbf{r})$ are fundamental parameters of a rigid molecular system with fixed nuclei whose settings determine the adiabatic electronic Hamiltonian and hence stationary states of such system. The correspondence rule which relates any given N and $v(\mathbf{r})$ to the ground state energy E_0 may be written in the form of the well-known variation principle of quantum mechanics for closed systems:

$$E_0(N, v) = \inf_{\Psi} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (2)$$

which operates with the energy functional defined for some specified class of test wave functions. Let Ψ_0 be a normalized test function which satisfies variation principle (2) at a given potential $v(\mathbf{r})$. In this case definition of electronic CP (1) takes form (3), according to which the quantity μ characterizes the ground

electronic state of an atom, molecule, or radical species in a given (not necessary equilibrium) geometric configuration of nuclei.

$$\mu = \frac{\partial}{\partial N} [\langle \Psi_0 | H | \Psi_0 \rangle]. \quad (3)$$

Unfortunately, Eq. (3) still provides no algorithm for calculation of electronic CP of a system. For this purpose, it is necessary either to formulate a rule for formal differentiation of the energy functional with respect to the number of electrons or to develop calculation schemes which do not involve such differentiation in the explicit form. It is now possible to perform only approximate calculation of electronic CP by the quadratic interpolation formula

$$\mu \approx -\frac{I^{(1)} + A^{(1)}}{2},$$

where $I^{(1)}$ and $A^{(1)}$ are, respectively, the ionization potential and electron affinity of the ground electronic state of a neutral system, which correspond to vertical processes occurring without change of geometric configuration [2].

On the basis of formal analogy between the definitions of electronic CP and of atomic EN according to Iczkowski and Margrave [3], Parr *et al.* [4] postulated that EN of any molecular system may be equated to the absolute value of electronic CP:

$$\chi = -\mu \approx \frac{I^{(1)} + A^{(1)}}{2}. \quad (4)$$

It should be emphasized that Parr *et al.* [4] considered EN to be a parameter of the ground electronic state; the authors did not raise the question so as to how does Eq. (4) apply to such imaginary species as substituents. This was done by Proft *et al.* [5] who were the first to make use of interpolation formula (4) for variation calculations of orbital ENs of substituents. However, the validity of such approach is not obvious, and it requires special discussion.

The approach is implicitly based on the assumption that valence state of a substituent may be simulated by the ground state of the same group of atoms in a nonequilibrium configuration reproducing standard geometry of the substituent in various molecules. Strictly speaking, the above assumption is invalid from the chemical point of view, at least for the following reason. A univalent substituent in diamagnetic molecules should possess a zero spin density, which is not the case of the ground state of the corresponding free radical having the same geometry.

Unfortunately, it is now impossible to speak unequivocally on the validity of using Eq. (4) for calculation of group ENs; therefore, we ought to confine ourselves to superficial consideration of this problem with methyl group as an example. The theory of covalent structures implies that the ground electronic state of methyl group having a pyramidal configuration is described by a determinant composed of doubly occupied C–H bond orbitals and unpaired electron orbital localized on the central atom. On a qualitative level, such description is reproduced in terms of the restricted Hartree–Fock procedure by a wave function allowing localization of closed-shell molecular orbitals via appropriate orthogonal transformation. In the framework of Van Vleck's orbital model [6], density matrices for valence state of methyl group can be built up from localized orbitals intrinsic to its ground electronic state, taking into account that hybridization of the unpaired electron orbital is fixed by the geometry and that it does not change in going from the ground to valence state. Van Vleck's model implies that unpaired electron, which is responsible for unsaturated valence of the group, occurs in a mixed spin state. Hence the N -electron density matrix for valence state of methyl group may be represented as follows:

$$D(\mathbf{x}; \mathbf{x}') = 1/2\Psi_{\alpha}(\mathbf{x})\Psi_{\alpha}^*(\mathbf{x}') + 1/2\Psi_{\beta}(\mathbf{x})\Psi_{\beta}^*(\mathbf{x}'), \quad (5)$$

where Ψ_{α} and Ψ_{β} are degenerate one-determinant wave functions of the ground state of a radical with different spin projections. Equation (5) indicates that the valence state energy of methyl group coincides with the energy of its ground electronic state having the same geometry. The first ionization potential of the ground state of methyl group is the energy of abstraction of unpaired electron. In keeping with Eq. (5), it coincides with the ionization potential of its valence state. Analogous reasonings also apply to electron affinity. Then, in the independent species approximation, the orbital CP of methyl group (which is the average energy of unpaired electron in Van Vleck's valence state) is equal to the electronic CP of the ground state of methyl radical with the same geometric configuration of nuclei. This conclusion seems to be valid for any univalent substituents, probably except for two-atom groups like OH with orbital-degenerate ground electronic states. However, its extension to substituents having two and more unsaturated valences is unlikely to be justified, for the energies of the ground and valence states of such systems, as well as of cations and anions derived therefrom, do not coincide with each other.

So far we discoursed in terms of the independent species model, for localized orbitals are the only point linking the chemical theory of covalent structures and quantum-mechanical description of stationary states of atoms and molecules. However, from the variation viewpoint the RHF wave function is far from being optimal. Therefore, it is unreasonable to absolutize Van Vleck's model considering it to be something restricting the level of variation calculation of orbital CP by interpolation formula (4).

Undoubtedly, electron correlation should affect electronic CP of a multielectron system. Insofar as correlation corrections to energy are taken into account by the perturbation theory, they can be interpreted, in principle, as interactions between localized elements of a covalent structure. There is no problem concerning interpretation of correlation effects while estimating electronic CP by the interpolation procedure, and these effects can be considered in terms of both perturbation theory and variation methods. We presumed that orbital EN of a univalent substituent is equal to the absolute value of its electronic CP at any level of quantum-chemical theory and performed nonempirical calculations of 26 univalent substituents having various structures. Our main goals were (1) to examine the effect of electron correlation on orbital ENs of univalent substituents and (2) to draw a nonempirical scale of group ENs and compare it with Mulliken's spectroscopic scale.

Quantum-chemical calculations of orbital electronegativities of univalent substituents. First of all, we must choose the procedure, basis set, and initial geometric parameters for calculation of $\chi_{1,G}$ by interpolation formula (4); it is convenient to rewrite the latter in the form of Eq. (6):

$$\chi_{1,G} \approx \frac{E(G^+) - E(G^-)}{2}. \quad (6)$$

Here, $E(G^+)$ and $E(G^-)$ are the electronic energies of radical cation and radical anion, respectively, calculated for standard geometric configuration of the substituent. These quantities are the energies of diamagnetic systems in the singlet state, which can be calculated by the RHF procedure with or without account taken of electron correlation. Generally speaking, the choice of the calculation scheme is optional; the only necessary condition is the use of an extended basis set including diffuse functions for correct description of anionic systems [7].

Proft *et al.* [5] calculated the energies of cations and anions derived from the corresponding radicals by the CISD/6-31++G(*d,p*) procedure with account taken of configurational interactions, using fixed standard geometric parameters. Both one- and two-electron replacements in one-determinant Hartree–Fock function were considered. The procedure, basis set, and geometric parameters used in [5] were optional since no systematic study of the effect of these factors on the resulting $\chi_{1,G}$ was performed. We examined the role of the above factors in various combinations with haloalkyl groups as examples. Analysis of the data in Table 1 showed that variation of $\chi_{1,G}$ in the series of isovalence-substituted systems is qualitatively reproduced with any basis set supplemented by diffuse functions provided that electron correlation is taken into account in one or another way. With the use of standard geometric parameters, mutual effects of atoms in a substituent can be taken into consideration only partially. As a result, $\chi_{1,G}$ values for substituents containing 3rd Period elements are overestimated (Table 1). The orbital EN of univalent substituents strongly depends only on the bond lengths between the central atom and other atoms of the group; variation of the other parameters almost does not affect $\chi_{1,G}$. Our results led us to choose the coupled cluster procedure CCSD/6-311++G(*d,p*) with account taken of one- and two-electron excitations, using optimized geometric configuration of nuclei which reproduced the geometry of AX_{*n*} substituent in HAX_{*n*} molecule. The optimal geometry of AX_{*n*} was found on the basis of the experimental A–X

bond lengths taken from [8]. The other geometric parameters were optimized by the Hartree–Fock procedure with the 6-311G(*d,p*) basis set. The calculations were performed using GAUSSIAN-94 program [9].

In terms of the given approach we calculated orbital ENs of 26 univalent substituents (see Table 2; $\varepsilon_{1,G}^{QC}$ are given in eV). Comparison of the data obtained by the CCSD/6-311++G(*d,p*) and HF/6-311++G(*d,p*) methods shows that the effect of electron correlation on orbital ENs of substituents can be taken into consideration by scaling the values calculated by the RHF procedure:

$$\chi_{1,G}^{CCSD} \text{ (eV)} = 1.04 + 0.86\chi_{1,G}^{HF} \text{ (eV)}. \quad (7)$$

In such a simple way, the results of the coupled cluster method are reproduced with an accuracy of 0.3 eV which is quite sufficient in calculations of EN. The correlation coefficient for the two sets of quantum-chemical data is equal to 0.976.

Thus, in the calculation of group ENs we can use the RHF procedure with subsequent scaling of the calculated values. The scaling coefficients depend on the selected basis set and method of considering electron correlation. Specifically, transformation (8) ($r = 0.978$) is valid for the 6-31++G(*d,p*) basis set [5].

$$\varepsilon_{1,G}^{CISD} \text{ (eV)} = 1.13 + 0.80\varepsilon_{1,G}^{HF} \text{ (eV)}. \quad (8)$$

Nonempirical scale of electronegativity. The results of quantum-chemical calculations given in Table 2 (eV) still do not form nonempirical scale of orbital ENs of substituents. In order to construct this scale it is necessary to find such scaling transformation which converts quantum-chemical ENs from eV to Pauling's thermochemical units (t.u.) as standard units for measuring EN and comparing different calculation schemes. No such task was set in [5]. The authors restrict themselves to qualitative description of the correlation between the results of their own calculations and known scales.

Let us compare the data (eV) given in Table 2 with spectroscopic $\chi_{1,G}^S$ values obtained by us in [10] in terms of the additivity approach based on Van Vleck's valence state model and principle of leveling of orbital CPs [see Table 2 in [10]: $\chi_{1,G}^S$ values (eV) were calculated by Eqs. (10)]. Obviously, quantum-chemical ENs of univalent substituents differ considerably from spectroscopic values. However, the deviations are systematic and are likely to result from the orbital compression effect which is not taken into account in spectroscopic ENs and hardnesses of elements used in the calculation of group ENs by the additive scheme

proposed in [10]. The reason is that the original formulation of Van Vleck's model reflects the concepts of 1930s, when interference and polarization were believed to be the only electron coupling effects influencing the energy of covalent bond between atoms. Detailed analysis of the energy of covalent bonding [12] shows that these concepts are, generally speaking, inaccurate. Coupling of electrons is always accompanied by compression of orbitals of the atoms being linked, which reduces the energy of the binding electron pair. Just this effect provides the main contribution to the energy of covalent bond. Nonempirical methods of quantum chemistry treat orbital compression with the aid of double or extended basis sets.

From the above viewpoint, hybrid orbitals of Van Vleck's atom are not atomic orbitals in the exact sense since they should reflect compression of atomic orbitals with regard to the number and multiplicities of bonds of the atom, i.e., depending on its valence state. Therefore, expansion of Van Vleck's valence state with respect to stationary states of the free atom and hence estimation of orbital ENs and hardnesses of atoms from spectral data are not quite correct. This is a probable reason for difference between spectroscopic and quantum-chemical ENs of substituents.

According to our data, the difference between spectroscopic and quantum-chemical EN of a given group is determined mainly by the nature and valence state of the central atom, while the effect of its environment in the group is insignificant. As an example, let us consider alkyl and haloalkyl radicals for which most extensive quantum-chemical data are available. As follows from Table 2, the quantity $\chi_{1,G}^S - \chi_{1,G}^{QC}$ for univalent substituents like CR_kHal_{4-k} is 3.1 ± 0.3 eV when $\chi_{1,G}^{QC}$ is calculated by the CCSD/6-311++G(*d,p*) or CISD/6-31++G(*d,p*) method. It is reasonable to presume that the average value of $\chi_{1,G}^{QC} - \chi_{1,G}^S$ for CR_kHal_{4-k} is determined mainly by orbital compression of the central atom and that it can be used to adjust spectroscopic EN of the atom C(*tetetete*, V_4)*. On the basis of the above assumptions we obtained rough estimates of quantum-chemical EN of quadrivalent carbon, which take into consideration orbital compression to a degree corresponding to the calculation scheme used for determination of electronic CP. In our cases the quantum-chemical EN of quadrivalent carbon is 4.9 eV. Analogous estimates (eV) can be

* Hereinafter we used Van Vleck's valence state identifier proposed by Mulliken [13], which indicates hybridization (*te* denotes tetragonal, sp^3 ; *tr* denotes trigonal, sp^2 ; and *di* denotes linear, sp) and valence state n (V_n) of an atom.

Table 1. Quantum-chemical electronegativities $\chi_{1,G}^{QC}$ of alkyl and haloalkyl groups (eV)

Group (G)	CISD 6-31++G(<i>d,p</i>) ^a [5]	CCSD	
		6-31++G(<i>d,p</i>) ^a	6-311++G(<i>d,p</i>) ^b
CH ₃	5.12	5.12	5.20
CH ₂ F	4.97	5.01	5.18
CHF ₂	5.25	5.30	5.44
CH ₂ Cl	4.89	4.92	5.06
CHCl ₂	5.12	5.15	5.20
CH ₂ Br		5.01	5.05
CHBr ₂		5.30	5.18
CHFCH ₃		4.50	4.68
CHClCH ₃		4.58	4.65
CHBrCH ₃		4.69	4.67

^a Calculated using standard geometric parameters.

^b Calculated using optimized geometric parameters.

obtained for trivalent nitrogen [N(*te²tete*, V_3): 7.5 (CCSD), 7.9 (CISD)] and phosphorus atoms [P(*s²ppp*, V_3): 4.5 (CISD)], as well as for bivalent oxygen [O(*te²te²tete*, V_2): 11.0 (CCSD), 10.7 (CISD)] and sulfur [S(*s²p²pp*, V_2): 5.7 (CCSD), 5.3 (CISD)]. It should be emphasized that arrays of quantum-chemical data necessary for determination of orbital ENs of the above atoms are very limited. Therefore, the given estimates are less reliable than for quadrivalent carbon.

Comparison of the $\chi_{1,A}^{QC}$ values thus obtained with Pauling's thermochemical atomic ENs (see Table 1 in [10]; $\chi_{1,A}^S$ values are given in parentheses) shows that quantum-chemical estimates of atomic ENs qualitatively reproduce the relations between ENs of different atoms, determined by Pauling [11]. In particular, the following EN series is observed for both levels of quantum-chemical treatment:

$$\chi_{1,P} \approx \chi_{1,C} \approx \chi_{1,S} < \chi_{1,N} < \chi_{1,O}$$

This is not accidental, for any reasonable physical scale of atomic ENs should correlate with Pauling's thermochemical scale which was derived in terms of a formal approach without using any valence state model. Therefore, we accept that scaling transformations converting EN from eV to t.u. may be defined as linear regressions of the quantity $\chi_{1,A}^{QC}$ with respect to Pauling's atomic ENs. Obviously, the regression coefficients should depend on the method of calculation of quantum-chemical ENs. For example, scaling transformations of orbital ENs calculated by the

CCSD/6-311++G(*d, p*) and CISD/6-31++G(*d, p*) methods look as follows:

CCSD/6-311++G(*d, p*):

$$\chi^{\text{QC}}(\text{t.u.}) = 2.1 + 0.17[\chi^{\text{QC}}(\text{eV}) - 2.8]; \quad (9)$$

CISD/6-31++G(*d, p*):

$$\chi^{\text{QC}}(\text{t.u.}) = 2.1 + 0.20[\chi^{\text{QC}}(\text{eV}) - 3.6]. \quad (10)$$

These transformations were derived from limited data samples which are now available. Therefore, the coefficients depend on the sample used, and they are to be refined as new data appear. The correlation coefficients between quantum-chemical and thermochemical ENs of Van Vleck's atoms are 0.986 for the CCSD/6-311++G(*d, p*) calculations and 0.975 for CISD/6-31++G(*d, p*).

Comparison of the quantum-chemical scale of group ENs with Mulliken's scale is complicated by the fact that the available spectroscopic values of orbital ENs and hardnesses of many elements have been determined with the use of improper valence state models, so that they should be refined. In terms of Van Vleck's spectroscopic model, valence states of trivalent nitrogen and phosphorus atoms, as well as of bivalent oxygen and sulfur atoms, should be built up from hybrid orbitals having a partial *s* order, which reproduce standard geometric bond configuration of an element in its compounds. Unfortunately, there are no published data for such valence states. For this reason we used in the calculations spectroscopic parameters of N(*te²tetete*, *V*₃) and O(*te²te²tete*, *V*₂) with tetrahedral configuration and of P(*s²ppp*, *V*₃) and S(*s²p²pp*, *V*₂) composed of nonhybridized orbitals (see Table 1 in [10]). Insofar as Van Vleck's orbital EN sharply increases with increase in the *s* order of the orbital responsible for unsaturated valence, spectroscopic ENs of N(*te²tetete*, *V*₃) and O(*te²te²tete*, *V*₂) are strongly overestimated relative to the thermochemical EN values of trivalent nitrogen and bivalent oxygen, while spectroscopic ENs of P(*s²ppp*, *V*₃) and S(*s²p²pp*, *V*₂) are underestimated relative to the corresponding thermochemical values. According to the data of [14], the use of hybrid orbitals reproducing standard bond configuration ensures negligible discrepancy between the spectroscopic and thermochemical ENs of nitrogen, oxygen, phosphorus, and sulfur. It is interesting that quantum-chemical ENs of trivalent nitrogen and phosphorus and bivalent oxygen and sulfur are consistent with Pauling's thermochemical values much better than are spectroscopic ENs of N(*te²tetete*, *V*₃), O(*te²te²tete*, *V*₂), P(*s²ppp*, *V*₃),

and S(*s²p²pp*, *V*₂). The reason is that corrections for orbital compression simultaneously eliminate errors arising from over(or under)estimation of the *s* order of hybrid orbitals of the above atoms.

Turning our attention to additive formulas relating orbital ENs of univalent chemical groups to valence state parameters of atoms {see Eqs. (10) in [10]}, we can see that group EN is affected mainly by errors in the determination of atomic ENs. According to the data of [14], the dependence of diagonal orbital hardnesses of Van Vleck's atom upon *s* order of the unsaturated valence orbital is much weaker than analogous dependence for the orbital EN. Moreover, orbital hardnesses are included in additive formulas as dimensionless factors with an order of magnitude of about 0.5. Therefore, the error in determination of orbital hardnesses of atoms should not exert an appreciable effect on spectroscopic orbital ENs of substituents. As concerns orbital ENs of elements, their corrected values expressed in thermochemical units via the scaling transformation

$$\chi^{\text{S}}(\text{t.u.}) = 2.1 + 0.4[\chi^{\text{S}}(\text{eV}) - 7.2] \quad (11)$$

should be similar to Pauling's thermochemical ENs. Transformation (11) was drawn on the basis of the data of [11, 14] for the states H(*s*, *V*₁), B(*trtrtr*, *V*₃), C(*tetetete*, *V*₄), F(*s²p²p²p*, *V*₁), Si(*tetetete*, *V*₄), Cl(*s²p²p²p*, *V*₁), and Br(*s²p²p²p*, *V*₁), for which the degree of orbital hybridization has been determined unambiguously. With the above in mind we believe that the error in determination of spectroscopic ENs of substituents by additive formulas proposed in [10] may be reduced considerably through the use of atomic ENs recalculated from Pauling's thermochemical ENs by Eq. (11). Atomic ENs (eV) corrected in such a way were given in [10] (see Table 4 in the cited paper).

Group ENs can be calculated both in eV with subsequent conversion to thermochemical units via Eq. (11) and directly in t.u. by substituting atomic ENs (t.u.) and orbital hardnesses of atoms (eV) into Eqs. (10) from [10]. The resulting spectroscopic ENs of univalent substituents are given in [10] (see Table 5 therein). In the present article, Table 2 contains quantum-chemical ENs (t.u., in parentheses) obtained by nonempirical variation procedures using interpolation formula (6). The Hartree-Fock ENs were scaled by Eqs. (7) and (8) in order to take into consideration electron correlation effect. The quantum-chemical data were converted from eV to t.u. via scaling transformations (9) and (10).

Table 2. Quantum-chemical electronegativities $\chi_{1,G}^{QC}$ of univalent substituents in eV and t.u. (in parentheses)

Substituent (G)	CCSD ^a	CISD ^b	HF ^c	HF ^d	Substituent (G)	CCSD ^a	CISD ^b	HF ^c	HF ^d
CH ₃	5.20 (2.51)	5.12 (2.40)	4.41 (2.46)	4.41 (2.31)	CHCH ₂	5.24 (2.51)	5.18 (2.42)	4.71 (2.51)	4.74 (2.36)
CH ₂ F	5.18 (2.50)	4.97 (2.37)	4.72 (2.51)	4.57 (2.34)	CHO	4.55 (2.40)	4.55 (2.29)	4.54 (2.48)	4.65 (2.35)
CHF ₂	5.44 (2.55)	5.25 (2.43)	5.23 (2.58)	5.08 (2.42)	COCl	5.69 (2.59)	5.73 (2.53)	5.73 (2.66)	5.89 (2.55)
CF ₃		6.30 (2.64)		6.24 (2.60)	COCH ₃		4.29 (2.24)		4.18 (2.27)
CH ₂ Cl	5.06 (2.48)	4.89 (2.36)	4.77 (2.52)	4.68 (2.35)	CONH ₂		4.67 (2.31)		4.63 (2.34)
CHCl ₂	5.20 (2.51)	5.12 (2.40)	5.10 (2.56)	5.10 (2.42)	CO ₂ H	5.77 (2.60)	5.86 (2.55)	5.71 (2.66)	5.91 (2.55)
CCl ₃		5.53 (2.49)		5.58 (2.50)	CO ₂ CH ₃		5.48 (2.48)		5.50 (2.48)
CH ₂ Br	5.05 (2.48)		4.81 (2.52)		CCH	8.36 (3.05)	8.21 (3.02)	8.12 (3.02)	8.05 (2.89)
CHBr ₂	5.18 (2.50)		5.09 (2.56)		CN	8.84 (3.13)	8.63 (3.11)	9.57 (3.24)	9.54 (3.13)
CH ₂ CH ₃	4.49 (2.39)	4.42 (2.26)	3.73 (2.36)	3.75 (2.20)	SiH ₃		4.61 (2.30)		4.22 (2.28)
CHFCH ₃	4.68 (2.42)		4.16 (2.42)		NH ₂	6.21 (2.68)	6.16 (2.61)	5.34 (2.60)	5.33 (2.46)
CHClCH ₃	4.65 (2.41)		4.25 (2.44)		NHCH ₃	5.20 (2.51)		4.43 (2.46)	
CHBrCH ₃	4.67 (2.41)		4.31 (2.45)		NO ₂		7.84 (2.95)		8.61 (2.98)
CH ₂ OH	4.24 (2.34)	4.14 (2.21)	3.79 (2.37)	3.80 (2.21)	PH ₂		5.05 (2.39)		4.71 (2.26)
CH ₂ OCH ₃	4.11 (2.32)		3.67 (2.35)		OH		6.95 (2.77)		5.59 (2.50)
CH ₂ SH	4.26 (2.35)	4.15 (2.21)	4.02 (2.40)	4.01 (2.25)	OCH ₃	6.84 (2.79)	5.73 (2.53)	6.24 (2.74)	4.57 (2.34)
CH ₂ SCH ₃	4.02 (2.31)		3.76 (2.36)		SH		5.69 (2.52)		5.14 (2.43)
CH ₂ NH ₂	3.50 (2.22)	3.39 (2.06)	3.02 (2.25)	3.05 (2.09)	SCH ₃	5.88 (2.62)	4.99 (2.38)	5.58 (2.64)	4.40 (2.31)

^a CCSD/6-311++G(*d,p*); optimized geometric parameters.

^b CISD/6-31++G(*d,p*); standard geometric parameters [5].

^c HF/6-311++G(*d,p*); optimized geometric parameters.

^d HF/6-31++G(*d,p*), standard geometric parameters [5].

The data in Table 2 indicate that $\chi_{1,G}^{QC}$ values calculated by the CCSD/6-311++G(*d,p*) and HF/6-311++G(*d,p*) methods using optimized geometric parameters of substituents coincide within 0.1 t.u. Thus the RHF calculation of orbital ENs of univalent substituents, followed by scaling via Eq. (7) to take

account of electron correlation, gives almost the same results as those obtained by the coupled cluster procedure involving one- and two-electron replacements. An analogous conclusion can be drawn for $\chi_{1,G}^{QC}$ values calculated by the CISD/6-31++G(*d,p*) and HF/6-31++G(*d,p*) [5] with the use of standard geometric

parameters of substituents. As in the previous case, scaling of the RHF values reproduces those obtained by direct calculation with an accuracy of 0.15 t.u.

Group ENs calculated by the CCSD/6-311++G(*d,p*) and CISD/6-31++G(*d,p*) procedures coincide within 0.15 t.u. except for OCH₃ and SCH₃ groups for which the discrepancy increases to 0.25 t.u. This may be due to the fact that Proft *et al.* [5] followed the formalistic postulate [4] that EN of any molecular system is equivalent to the absolute value of its electronic CP; they considered ionization of OCH₃ and SCH₃ groups to the lowest triplet state using the unrestricted Hartree–Fock procedure for calculation of cations. By contrast, we leaned upon Van Vleck's valence state model and considered cations in a hypothetical singlet state with doubly occupied *p* orbital of the central atom, which corresponds to vertical ionization of the radical valence state.

Finally, let us consider spectroscopic ENs of univalent substituents, calculated by the additive scheme {Eqs. (10) in [10]} from refined values of orbital ENs of elements. As reference, we select nonempirical group ENs calculated by the CCSD/6-311++G(*d,p*) procedure, which is the most rigorous among the variation approaches used. Table 2 shows that spectroscopic and quantum-chemical ENs coincide within 0.1 t.u. for 20 of the examined substituents. A greater deviation is observed only for difluoromethyl group, for the principle of leveling of orbital CPs of a bond slightly overestimates the effect of C–F bonds on orbital EN of the central atom in the series of fluoro-substituted methyl groups.

A good agreement between the spectroscopic and quantum-chemical data supports the assumption that orbital EN of a univalent substituent may be equated to the absolute value of electronic CP of its ground electronic state and can be calculated by nonempirical variation methods of quantum chemistry using interpolation formula (6). The calculations can be performed by both coupled cluster procedure and RHF method with an extended basis set including diffuse functions. In the latter case, corrections for electron correlation (eV) are introduced through linear scaling of $\chi_{1,G}^{\text{HF}}$, which can be included in the scaling transformation converting quantum-chemical ENs to thermochemical units. A combination of Eq. (7) with the transformation

$$\chi^{\text{CCSD}}(\text{t.u.}) = 2.1 + 0.17[\chi^{\text{CCSD}}(\text{eV}) - 2.8]$$

[see Eq. (9)] gives the scaling transformation

$$\chi^{\text{HF}}(\text{t.u.}) = 2.1 + 0.15[\chi^{\text{HF}}(\text{eV}) - 2.0],$$

which converts orbital ENs calculated by the HF/6-311++G(*d,p*) method to thermochemical units with simultaneous correction for electron correlation. In keeping with our data, the results of calculation of group ENs by the above relatively simple scheme almost do not differ from the EN values obtained by the CCSD/6-311++G(*d,p*) procedure. The linear scaling method can also be applied to description of orbital compression in terms of Van Vleck's valence state model. As follows from the data in Table 2, the effect of orbital compression on orbital ENs of atoms and substituents (expressed in eV) can be taken into account by scaling of the spectroscopic values using the following formulas:

CCSD/6-311++G(*d,p*):

$$\chi^{\text{QC}}(\text{eV}) = 2.8 + 2.35[\chi^{\text{S}}(\text{eV}) - 7.2];$$

CISD/6-31++G(*d,p*):

$$\chi^{\text{QC}}(\text{eV}) = 3.6 + 2.00[\chi^{\text{S}}(\text{eV}) - 7.2].$$

These formulas are obtained by combination of Eq. (11) with scaling transformations (9) and (10), respectively. The conclusion clearly follows from the fact that spectroscopic and quantum-chemical ENs of univalent substituents, expressed in t.u., almost coincide with each other. It should be noted that our results emphasize once more the significance of Pauling's thermochemical units as standard units for measurement of EN, which do not depend on specific details of the calculation scheme and valence state model. Therefore, these units are the most convenient for comparing different scales of group ENs and analyzing models and methods used in the calculation of electronegativity.

An important point is that the above conclusions should be regarded as preliminary since scaling transformations (9) and (10) were derived from small arrays of data and, strictly speaking, they are not statistically reliable. Moreover, additional refinement is necessary for spectroscopic values of orbital ENs and hardnesses of atoms, which are used in the calculation of group ENs by additive schemes. Extension of the array of quantum-chemical data and determination of spectroscopic parameters of atoms in all Van Vleck's valence states intrinsic thereto are the most urgent problems in the field under study at present stage of its development.

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