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Charge-Overlap Study of Multiple Metal–Metal Bonding and Conjugation in Linear Chains of Transition-Metal Atoms

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For a comparative study of bonding, the d^{n}sp excited configuration, pertinent to linear digonal hybrids, was imposed on metals of three transition series. Computations of σ, π, and δ overlap of the s, p, and d orbitals in this configuration were made for selected metals, at the usual metallic distance, the distance in A_3B superconducting alloys, and the distance for known multiple metal bonds in complexes. The computation made use of single-ζ Slater orbitals derived from the same Burns rule for all. Subsequently, molecular orbital calculation of σ, π, and δ bonding for a repeating unit, $-(M_2)-$ in an infinite chain was made by using an extended Hückel method and the Mulliken–Wolfsberg and Helmholz approximation. The (same) parameter, $K = 1.75$, used for all metals was first tested for N_2 and P_2. The bond stabilization relative to the ground-state atoms, proportional to overlap, was used to approximate the bond dissociation energy. A new attempt was made to justify and to delineate the approximation involved and to show that the neglected two-electron integrals as well as the nuclear repulsion tend to cancel. Coulomb integrals were approximated by valence-orbital ionization energies (VOIE's), which for self-consistency were all obtained from existing *z*-series expansion of the Hartree–Fock SCF energies of the atoms and their ions of appropriate configuration. The d^{n}sp configuration energies were also obtained from the same HF–SCF calculations. In cases where data were not available and for the third series the d^{n}sp energies were obtained from weighted averages of spectroscopic term energies given by Moore. Overlap data here support dp hybridization assisted by sp in bonding that is principally dσ plus dπ and dδ. The bond strength as well as bond order for a chain peaks at group 6, drops at the first column of group 7, and rises again at group 8. The relative bond strength for dσ vs. dπ vs. dδ bonds was estimated by the ratio of relative stabilizations. Pictures of conjugate bonds and their resonance in a chain, consistent with the translational symmetry of the repeating unit, $-(M_2)-$, and with the conservation of azimuthal angular momentum were drawn. The study suggests that, for a chain of neutral transition-metal atoms, the most favorable multiple bonding occurs for group 5 and group 6 elements (more so for the second series than for the first), the largest number of resonance-conjugation hybrids exists for group 5, and the highest bond order occurs for group 6 atoms.

Introduction

Since the discovery of the first metal–metal quadruple bond[1] (in the $[Re_2Cl_8]^{2-}$ ion), there has been extensive experimental and theoretical interest in multiple metal bonds in transition-metal complexes. This is evident in most recent works and reviews.[2–9] The bonds range from triple[5,10,11] to sextuple,[12,13] involving mostly dinuclear or trinuclear complexes coordinated with a large number (4 or more) of conventional ligands (such as halide, sulfate, phosphate, etc.), and the metals are in low to medium positive oxidation states. The metal ions studied are from the first transition series (V,[14] ,Cr[15–17] Sc[18]), from the second transition series (Zr,[19] Mo,[16,20,21] Tc[22]), and from the third transition series (W,[16,19,20,23] Re[1,24,25]). Attempts to understand such multiple metal bonding have ranged from the simple d-orbital overlap of Cotton and Haas[26] to the extended Hückel molecular orbital theory of Hoffmann[27–29] or to the sophisticated Fenske–Hall LCAO–MO method[30] and SCF–Xα–SW calculations.[7,8,12,21,31]

While the breakthrough of the Wernerian concept of classical metal–ligand coordination is impressive, a few questions of interest remain:

1. What are other possible candidates for (multiple) metal–metal bonding among these transition series, especially the missing element in group 5, i.e., Nb and Ta, and the missing element in group 7, i.e., Mn?

2. What is the prospect for multiply bonded polynuclear complexes beyond di- and trinuclear complexes? This question is of special interest in view of recent interest in linear metal chain compounds.[32,33]

3. What about a chain of neutral metal atoms in metallic states even though the carbonyl complexes for neutral metal atoms contain mostly long and weak single metal–metal bonds? This is pertinent because in A15 (β-tungsten structure) compounds[34] (e.g., V_3Si) "linear chain integrity" exists among the A atoms, which have interatomic V–V distances (2.35–2.44 Å) shorter than the usual metallic radii. Also, it may be a coincidence, but the most frequently observed A atoms in A_3B

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Table I. Charge-Overlap Integrals between *First-Series* Transition-Metal Atoms ($d^n sp$ Configuration)

		1	2	3	4	5	6	7	8	9	10
metal	R, Å	$S(4s4s)$	$S(4p\sigma 4p\sigma)$	$S(4p\pi 4p\pi)$	$S(4s4p\sigma)$	$S(4s3d\sigma)$	$S(3d\sigma 3d\sigma)$	$S(4p\pi 3d\pi)$	$S(3d\pi 3d\pi)$	$S(3d\delta 3d\delta)$	$S(4p\sigma 3d\sigma)$
Sc	2.878	0.337	−0.052	0.630	0.607	0.071	0.059	0.043	0.029	0.004	−0.005
	2.30	0.495	−0.306	0.742	0.614	0.078	0.129	0.045	0.101	0.019	−0.031
Ti	2.648	0.336	−0.043	0.624	0.608	0.072	0.055	0.043	0.026	0.003	−0.004
	2.50	0.378	−0.109	0.655	0.616	0.073	0.071	0.044	0.039	0.006	−0.010
	2.30	0.437	−0.204	0.698	0.621	0.077	0.098	0.046	0.063	0.010	−0.021
V	2.448	0.338	−0.034	0.619	0.608	0.066	0.052	0.043	0.024	0.003	−0.001
	2.35	0.367	−0.079	0.641	0.617	0.070	0.063	0.043	0.032	0.005	−0.007
	2.20	0.415	−0.156	0.676	0.624	0.074	0.084	0.045	0.049	0.008	−0.015
Cr	2.372	0.309	0.024	0.589	0.601	0.060	0.039	0.040	0.017	0.003	0.004
	2.34	0.318	0.008	0.597	0.605	0.061	0.042	0.041	0.019	0.003	0.002
	1.97	0.442	−0.190	0.692	0.627	0.072	0.093	0.045	0.057	0.009	−0.019
Mn	2.356	0.266	0.101	0.548	0.580	0.039	0.026	0.036	0.010	0.001	0.011
	2.25	0.298	0.049	0.576	0.595	0.056	0.034	0.038	0.014	0.002	0.006
Fe	2.340	0.226	0.171	0.506	0.553	0.044	0.015	0.032	0.006	0.001	0.017
Co	2.324	0.192	0.232	0.465	0.526	0.033	0.010	0.029	0.003	0.000	0.046
Ni	2.308	0.165	0.280	0.428	0.494	0.026	0.006	0.025	0.001	0.000	0.023

Table II. Charge-Overlap Integrals between *Second-Series* Transition-Metal Atoms ($d^n sp$ Configuration)

		1	2	3	4	5	6	7	8	9	10
metal	R, Å	$S(5s5s)$	$S(5p\sigma 5p\sigma)$	$S(5p\pi 5p\pi)$	$S(5s5p\sigma)$	$S(5s4d\sigma)$	$S(4d\sigma 4d\sigma)$	$S(5p\pi 4d\pi)$	$S(4d\pi 4d\pi)$	$S(4d\delta 4d\delta)$	$S(5p\sigma 4d\sigma)$
Y	3.232	0.348	−0.184	0.687	0.586	0.123	0.149	0.054	0.106	0.019	−0.043
Zr	2.908	0.376	−0.210	0.700	0.590	0.120	0.156	0.053	0.117	0.022	−0.046
	2.74	0.418	−0.275	0.728	0.589	0.119	0.174	0.051	0.151	0.031	−0.054
Nb	2.684	0.390	−0.216	0.703	0.593	0.116	0.157	0.052	0.117	0.022	−0.047
	2.56	0.423	−0.268	0.725	0.592	0.115	0.171	0.050	0.145	0.029	−0.053
	2.30	0.493	−0.378	0.771	0.578	0.099	0.187	0.045	0.214	0.052	−0.062
Mo	2.592	0.374	−0.179	0.686	0.597	0.112	0.143	0.053	0.097	0.017	−0.041
	2.46	0.411	−0.237	0.712	0.597	0.112	0.162	0.049	0.126	0.024	−0.049
	2.07	0.521	−0.412	0.785	0.576	0.085	0.186	0.099	0.235	0.061	−0.064
Tc	2.542	0.349	−0.127	0.662	0.598	0.106	0.124	0.052	0.075	0.012	−0.034
	2.12	0.473	−0.326	0.750	0.592	0.100	0.182	0.047	0.174	0.038	−0.057
Ru	2.492	0.327	−0.079	0.640	0.596	0.100	0.105	0.052	0.058	0.008	−0.026
	2.25	0.399	−0.197	0.695	0.603	0.107	0.147	0.098	0.102	0.018	−0.043
Rh	2.504	0.288	−0.006	0.605	0.590	0.089	0.079	0.051	0.038	0.005	−0.014
Pd	2.566	0.237	0.087	0.555	0.569	0.073	0.050	0.048	0.021	0.002	0.000

(A15-type) compounds are[35] V, Cr, Nb, Mo, and Ta, in striking parallel to those observed in multiple metal–metal-bonded complexes.

4. What would the relative contribution[11,36] from a δ vs. π or σ bond to bond strength be?

5. What is the possibility of bond conjugation say, hypothetically, between alternating quadruple and double bonds or between single and triple bonds etc. if there are indeed multiple bonds in a linear complex or in a metal or in an alloy?

The answer to question 1 requires a comparative study of *all* three series of transition metals and their complexes. A theoretical study carried to high sophistication would be prohibitive, and unless a suitable quantity can be identified from comparison, the results may not be meaningful. Answers to questions 2 and 3 require the studies of one-dimensional metals, which, if carried to band structure models, would lose some of the chemical bonding insight we desire. However, linear structures are of basic interest because linear digonal hybrids appear not to have been studied while tetragonal and octahedral hybrids for metal complexes are well studied. The answer to question 4 requires delineation of σ, π, and δ bondings and finding their strengths. The answer to question 5 would depend on what parameter we use to describe conjugation-resonance energy or resonance structure etc.

Scope of Work and the Philosophy and Method of Calculation

We do not pretend to be able to answer all of the aforestated large questions. Rather, we hope to shed some light on these problems by concentrating on the study of linear digonal bonding. We consider a single repeating unit, $-(M_2)-$ in an infinite linear chain, imposing the same excited configuration, $d^n sp$, of the metal for all to facilitate comparison. We do this for the eight metals in the first transition series from Sc to Ni and for the six metals in the second series from La to Pt. We attempt to determine whether the bond stabilization energy is able to compensate for the excitation energy (exciting to the $d^n sp$ state, which is pertinent for digonal sp or dp hybridization).

We compute charge-overlap integrals for s, p, and d orbitals up to δ overlap at several atomic separations of interest (Tables I–III) and construct σ-, π-, and δ-symmetry orbitals, and then essentially we use an extended Hückel method[27] in solving the secular determinant for molecular orbital energy and molecular orbital eigenfunctions

$$|H_{ij} - \epsilon S_{ij}| = 0 \qquad (1)$$

where i and j stand for symmetry-adapted and normalized orbitals, Ψ_i and Ψ_j, viz.

$$\Psi_i, \Psi_j = (\Phi_a \pm \Phi_b)/[2(1 \pm S_{ab})]^{1/2} \qquad (2)$$

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Table III. Charge-Overlap Integrals between *Third-Series* Transition-Metal AToms (d^nsp) Configuration)

metal	R, Å	1 S(6s6s)	2 $S(6p\sigma 6p\sigma)$	3 $S(6p\pi 6p\pi)$	4 $S(6s\sigma 6p\sigma)$	5 $S(6s5d\sigma)$	6 $S(5d\sigma 5d\sigma)$	7 $S(6p\pi 5d\pi)$	8 $S(5d\pi 5d\pi)$	9 $S(5d\delta 5d\delta)$	10 $S(6p\sigma 5d\sigma)$
La	3.380	0.395	−0.323	0.747	0.548	0.163	0.207	0.044	0.260	0.065	−0.084
Hf	2.884	0.060	0.346	0.090	0.189	0.018	−0.003	0.016	−0.003	−0.002	0.054
Ta	2.686	0.085	0.386	0.114	0.228	0.025	0.003	0.021	0.000	−0.001	0.064
	2.63	0.095	0.398	0.125	0.246	0.029	0.006	0.027	0.000	0.000	0.069
	2.35	0.158	0.445	0.189	0.343	0.053	0.025	0.044	0.008	0.001	0.094
W	2.608	0.086	0.391	0.118	0.234	0.025	0.002	0.022	0.000	−0.001	0.064
	2.30	0.155	0.446	0.190	0.342	0.051	0.023	0.043	0.007	0.001	0.092
	2.16	0.196	0.450	0.232	0.393	0.067	0.039	0.057	0.014	0.001	0.098
Re	2.566	0.082	0.388	0.116	0.229	0.023	0.000	0.020	−0.001	−0.001	0.062
	2.40	0.114	0.426	0.152	0.286	0.035	0.011	0.030	0.003	0.000	0.077
	2.18	0.173	0.450	0.213	0.368	0.057	0.028	0.048	0.009	0.001	0.093
Os	2.520	0.078	0.387	0.116	0.226	0.021	−0.001	0.021	−0.002	−0.001	0.060
	2.35	0.112	0.427	0.153	0.285	0.034	0.010	0.029	0.002	0.000	0.075
Ir	2.530	0.066	0.370	0.104	0.205	0.017	−0.006	0.015	−0.004	−0.002	0.060
Pt	2.590	0.049	0.337	0.085	0.169	0.011	−0.016	0.012	−0.007	−0.003	0.042

For σ symmetry, there are three orbitals, $\Psi_{i,j} = s\sigma_g$, $p\sigma_g$, and $d\sigma_g$, which interact making 3 × 3 secular determinants. Similarly, there are $s\sigma_u$, $p\sigma_u$, and $d\sigma_u$. For π symmetry, there are simply $p\pi_g$, $d\pi_g$, $p\pi_u$, and $d\pi_u$, making 2 × 2 secular determinants. For δ symmetry there are $d\delta_g$ and $d\delta_u$.

We use the Mulliken–Wolfsberg–Helmholz[37,38] method of approximating the Coulomb integrals by the valence-orbital ionization energy (VOIE) of the corresponing s, p, and d (l = 0, 1, and 2) orbitals, i.e.

$$H^a_{nl,nl} = H^{nl}_{a,a} \simeq -nl(\text{VOIE}) \qquad (3)$$

for the nl orbital of atom a. Following the same method, we approximate the resonance integral by

$$H_{ab} = KS[\tfrac{1}{2}(H_{aa} + H_{bb})] \qquad (4)$$

where the final choice, $K = 1.75$, was determined by using it with this method to calculate the known dissociation energy of N_2 and P_2 (Table IV). The theoretical basis and method for estimating bond dissociation energy as proportional to overlap are detailed in the Appendix.

There are several justifications for our severe approximation. In a recent study[7] comparing the method of d-orbital overlap, the Fenske–Hall LCAO–MO method and SCF–X–SW calculation, Bursten, Cotton, and Stanley concluded that the simple d overlap[26] provides the most important contribution to bonding. To this d-orbital overlap we have added the modulating effect of s and p overlaps by mixing s, p, and d through the solution of (3 × 3 and 2 × 2) secular determinants. This simple one-electron molecular orbital treatment, while giving perhaps too much weight to ionic states, naturally and simultaneously takes into account ds and dp digonal hybridization. It circumvents a two-electron valence-bond treatment by using a rather arbitrary digonal hybrid-bond orbital[39] such as $(s_a \pm p_a)/2^{1/2}$ or $(s_a \pm \alpha p_a)/[2(1 + \alpha^2)]^{1/2}$. And for the case of σ plus additional π bonding, it circumvents a four-electron (two σ electrons and two π electrons) valence-bond treatment. Although they were not treated by Kimball,[40] by symmetry, sf_σ and $d_\sigma f_\sigma$ also should contribute to digonal hybridization (f_σ, similar to p_σ, belongs to the Σ_u^+ irreducible representation in the $D_{\infty h}$ point group[41]). However, among all of the metals in the three transition series we studied, only lanthanum has an observed, assigned excited state involving an open-shell f orbital,[42] i.e., 5d6s4f and $5d^24f$. Therefore, we did not include f orbitals in general.

Table IV. Calibration of Parameter K

		N_2	N_2	N_2	P_2
R, Å		1.48	1.24	1.10	1.88
“D_e”,[a] eV	$K = 1.75$	7.96	9.34	9.76	8.12
	$K = 2.0$	13.2	16.3	17.5	13.3
	$K = 1.5$	3.46	3.06	2.52	3.36
“D_e”(exptl),[b] eV				9.75	5.03
D_e(SCF),[c] eV				5.27	7.90

[a] This “D_e” is an approximation and is better referred to as bonding orbital stabilization. See the Appendix. The result for N_2 is absurd for $K = 1.5$ relative to shortening of distance. The conformation of N_2 is $(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)^2$. The configuration of P_2 is $(\sigma_g3s)^2(\sigma_u3s)^2(\pi_u3p)^4(\sigma_g3p)^2$. $\zeta_{2s} = 1.875$, $H_{2s2s} = -25.56$ eV; $\zeta_{2p} = 1.650$, $H_{2p2p} = -13.19$ eV; $\zeta_{3s} = 1.816$, $H_{3s3s} = -18.77$ eV; $\zeta_{3p} = 1.300$, $H_{3p3p} = -10.11$ eV. [b] For N_2, the result is based on dissociation into $^4S + {}^2D$ (both $2s^22p^3$ configuration). See G. Herzberg, “Spectra of Diatomic Molecules”, Van Nostrand, New York, 1950, pp 448 ff, 551. [c] Theoretical self-consistent field calculation. For N_2, see H. F. Schaefer III, “The Electronic Structure of Atoms and Molecules”, Addison-Wesley, Reading, MA, 1972, p 149; for P_2 the result is based on $D_e = c\eta\bar{I}$ with average $\bar{c} = 0.342$ for six homopolar diatomic molecules. See R. S. Mulliken and W. C. Ermler, “Diatomic Molecules–Results of ab Initio Calculations”, Academic Press, New York, 1977, p 133.

We wish to stress here that we use only spectroscopically observed real states such as d^nsp. And, as a byproduct of this work, we have computed (see below) the average energy of such d^nsp configurations as well as the valence-orbital ionization potentials for s, p, and d electrons in these configurations. We have, however, not calculated the energy to charge self-consistency because of the immense extra effort required for iteration. Instead we assume that excitation to the d^nsp configuration already, to a first-order approximation, gives better electron correlation and provides a favorable electron distribution for linear digonal bonding. Furthermore, by imposition of the d^nsp configuration for *all* metal atoms, the result also gives a measure of relative ease with which they form linear digonal bonds. This we fell is sufficient for our purpose because our interest lies in comparative study instead of in the absolute values of the energies. Aside from this, the approximate nature of the one-electron extended Hückel treatment and the Mulliken–Wolfsberg–Helmholz method might not justify the extra effort. Our intellectually honest hope is for cancellation of errors by a suitably chosen way of analyzing the data, as explained in the Appendix. This Appendix deals

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with the theoretical approximation of bond energy. We also hope that, by comparison of the relative values in a series of metals, the errors will subtract out and a true trend will emerge. It should be noted at this point that, while the extended Hückel and Mulliken–Wolfsberg–Helmholz methods and their improvements have been used extensively and recently,[10,29,38,43–46] the required VOIE data have received little new imput since the early study of Basch, Viste, and Gray[47] in 1966 for the first transition series. Even the old data have a great deal of diversity depending on the author's taste, and the results of theoretical calculations differ from author to author. We list examples as well as the diverse energies of the excited $d^n sp$ configuration given by various authors. These are compared with the values used in this work (see Table V). It is noted that the observed states for a configuration, as given in Moore's tables,[42] are seldom complete and the weighted average energies obtained for these configurations, while ostensibly based on experimental data, are not to be taken as genuine, and we therefore caution against mixing exact experimental values and approximate theoretical values in the analysis of data. This is because of the reliance on error cancellation (or cancellation of neglected terms) in the approximate method used. (See Appendix.)

Because of our emphasis on comparison within the same transition-metal series and between different series, the internal self-consistency and uniformity of parameters used are of paramount importance in our work. Therefore, we have avoided the use of existing but diverse data on VOIE, configuration energies, and Slater orbital exponents and do the following:

i. Generate all of the VOIE values used from the polynominal Z expansions tabulated for *nonrelativistic* SCF Hartree–Fock calculations[48] and equate them to the Coulomb integrals. We obtain

$$\begin{aligned} \text{s-VOIE} &= E(d^n p) - E(d^n sp) \simeq -H_{ss} \\ \text{p-VOIE} &= E(d^n s) - E(d^n sp) \simeq -H_{pp} \\ \text{d-VOIE} &= E(d^{n-1} sp) - E(d^n sp) \simeq -H_{dd} \end{aligned} \qquad (5)$$

by first calculating the energies E. We emphasize the nonrelativistic work since tabulations of relativistic calculations are not available. Thus, the VOIE's are not to be combined with other values, however genuine and true the experimental values, that contain relativistic (mass, Breit magnetic correction, etc.) effects. They are to combine (subtract or add) with molecular orbital energies *derived from themselves* so that the neglected relativistic and other effects will essentially cancel out. We obtained VOIE's for Sc to Ni in the first series and for Y to Ru in the second series. The expansions for the rest of the second series (Rh, Pd) and for all of the third series are not available.

ii. Generate all of the configuration excitation energies, ΔE, for $d^n sp$ on the basis of the same tabulation;[48,49] viz., obtain

$$E(d^n sp) = E(M^* d^n sp) - E(M^0\ d^n s^2 \text{ or } d^{n+1} s) \qquad (6)$$

after calculating the energies of E. Again, we could do this only up to Ru in the second series. Therefore, we have performed extended Hückel molecular orbital calculations only up to Ru (Tables VI and VII). Although we have computed the average configuration energies of $d^n sp$ for the third transition series from spectroscopic data given by Moore and compiled VOIE and other data for the third transition series (Table VIII), we did not use them in molecular orbital calculations. This would not be comparable to the other calculations and would be misleading. We have, however, computed overlap integrals for the third series using the Slater orbital exponents derived by the *same* rules[50] *as* the rest.

iii. Use the *same* set of rules of Burns[50] to get single-ζ Slater orbital exponents, and use such ζ's to obtain all overlap integrals, using the integral tables[51] of Boudreaux, Cusachs, and Dureau. While Burn's single-ζ values may not be the most accurate, they cover the whole range of transition-metal series. We decided to sacrifice some accuracy in the interest of internal self-consistency.

iv. Use the same $K = 1.75$ for the resonance integral in eq 4 for both the first and second transition series and for σ, π, and δ orbitals. In N_2 and P_2, it produced reasonable results (Table IV) but probabaly overestimated the bond stabilization for the transition metals. But, if the value of one of the metals can be obtained experimentally, the rest can be extrapolated with reasonable assurance on the basis of the relative values given here, with the assumption, of course, that the proportionality to overlap is valid to the same extent in all metals.

Results

After solution of the secular determinant in (1), we obtained energies for 12 molecular orbitals: $\sigma_g nd$, $\pi_u nd$, $\delta_g nd$, $\delta_u nd$, $\pi_g nd$, $\sigma_g(n+1)s$, $\sigma_u(n+1)s$, $\pi_u(n+1)p$, $\sigma_g(n+1)p$, $\pi_g(n+1)p$, $\sigma_u(n+1)p$. The d molecular orbitals are the lowest, followed by the s and p. The exact order within the same parentage depends on the elements and interatomic distances. These results confirm the theory that d orbitals are principally responsible for bonding. We have purposely used the parent atomic d orbital to help designate the molecular orbitals. We then computed the bond stabilization energy of $-(M_2)-$ by taking the electronic energies of occupied molecular orbitals and subtracting the VOIE of the starting atomic configuration electrons ($d^n sp$):

$$\begin{aligned} \Delta E^*(\text{bonding stabilization}) &= \\ E(-M_2-) - 2E(M^*\ d^n sp) &= \\ \textstyle\sum_\Lambda N_\Lambda \epsilon_\Lambda - 2(n\epsilon_D + \epsilon_s + \epsilon_p) + Z^2/R_{ab} &= \\ \textstyle\sum_\Lambda N_\Lambda \epsilon_\Lambda - 2(nH_{DD} + H_{ss} + H_{pp}) & \end{aligned} \qquad (7)$$

where N_Λ is the electron occupation number of molecular orbital Λ and where replacement of $\epsilon = -\text{VOIE}$ by the Coulomb integral, $H^j_{aa} = H_{jj}$ (j = s, p, d), is operationally justified because the difference in the Coulomb attraction term will approximately cancel out the nuclear repulsion term, Z^2/R_{ab}, as explained in detail in the Appendix (eq A-11 and A-13–A-16). Similarly, if VOIE is used for $-\epsilon$ (as done here), the implication is that the Coulomb attraction term in ϵ_Λ (see eq A-15) will cancel out the nuclear repulsion. Also, in this way the errors involved in obtaining H_{jj} will cancel those in the derived energy, ϵ_Λ. The neglected two-electron Coulomb and exchange integrals for atoms as well as for the molecule, in this approximation, are given in the Appendix (eq A-11).

This ΔE^* is the bond stabilization with respect to the excited $d^n sp$ configuration. It is the stabilization we gain by exciting

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(51) E. A. Boudreaux, L. C. Cusachs, and L. D. Dureau, "Numerical Tables of Two-Center Overlap Integrals", W. A. Benjamin, New York, 1970.

Table V. d^nsp Configuration Energy (eV), VOIE (eV), and Single-ζ Slater Orbital Exponents (Ground-State Values in Parentheses)

a. First-Series Transition-Metal Atoms

	VOIE ≅ $-H_{dd}$				VOIE ≅ $-H_{pp}$			VOIE ≅ $-H_{ss}$						d^nsp energy			
	this work[a]	Moore[b]	Baste, Viste, Gray[c]	others[d]	this work[a]	Baste, Viste, Gray[c]	others[d]	this work[a]	Baste, Viste, Gray[c]	others[d]	ζ_{4s}	ζ_{4p}	ζ_{3d}	Baste, Viste, Gray[c]	this work[a]	Syrkin, Dyatkina[e]	Moore[b]
Sc	6.73 (9.25)	9.53	7.94	(5.60)	2.08 (...)	3.95	(2.95)	5.31 (5.71)	7.54	(6.15)	1.437 (0.95)	0.750 (...)	2.100 (2.07)	2.50	4.23	1.95	2.38
Ti	7.73 (11.97)	10.62	9.00	(5.00)	2.07 (...)	4.26	(3.35)	5.52 (5.98)	8.18	(5.90)	1.562 (1.08)	0.825 (...)	2.316 (2.28)	2.68	5.77	1.95	3.55
V	8.47 (13.88)	10.59	10.09	(5.90)	1.95 (...)	4.51	(3.75)	5.71 (6.26)	8.75	(6.85)	1.687 (1.45)	0.900 (...)	2.523 (2.50)	3.50	7.58	2.04	4.56
Cr	9.29 (15.51)		11.22	(7.00)	1.82 (...)	4.72	(3.75)	5.78 (6.53)	9.26	(7.25)	1.812 (1.32)	0.975 (...)	2.750 (2.72)	2.43	0.49	3.08	5.51
Mn	10.08 (17.41)	15.10	12.37	(8.0)	1.63 (...)	4.88		5.90 (6.80)	9.70	(7.0)	1.937 (1.45)	1.050 (...)	2.966 (2.94)	3.71	12.93	2.25	5.88
Fe	10.98 (17.68)	13.50	13.55	(10.0)	1.68 (...)	4.99		6.20 (7.07)	10.09	(7.0)	2.062 (1.57)	1.125 (...)	3.183 (3.15)	2.93	10.88	2.34	5.38
Co	11.55 (18.50)	13.24	14.78	(10.0)	1.54 (...)	5.06		6.36 (7.34)	10.41	(7.4)	2.187 (1.70)	1.200 (...)	3.400 (3.37)	3.40	10.11	2.90	4.86
Ni	12.13 (19.32)	...	16.02	(10.1)	1.28 (...)	5.07		6.28 (7.62)	10.66	(8.9)	2.312 (1.82)	1.275 (...)	3.616 (3.58)	3.85	9.32	3.16	4.67

b. Second-Series Transition-Metal Atoms

	VOIE ≅ $-H_{dd}$ this work[a]	VOIE ≅ $-H_{pp}$ this work[a]	VOIE ≅ $-H_{ss}$ this work[a]	ζ_{5s}	ζ_{5p}	ζ_{4d}	d^nsp energy this work[a]		VOIE ≅ $-H_{dd}$ this work[a]	VOIE ≅ $-H_{pp}$ this work[a]	VOIE ≅ $-H_{ss}$ this work[a]	ζ_{5s}	ζ_{5p}	ζ_{4d}	d^nsp energy this work[a]
Y	3.82 (6.80)	1.16 (...)	4.09 (5.44)	1.49	0.72	1.825	5.72	Tc	9.08 (14.69)	0.81 (...)	4.69 (6.26)	1 89	0.96	2.47	12.24
Zr	4.98 (9.25)	1.03 (...)	4.26 (5.71)	1.59	0.78	1.98	7.03	Ru	10.20 (15.51)	0.77 (...)	4.97 (6.53)	1.99	1.02	2.63	0.82
Nb	6.13 (11.15)	0.86 (...)	4.23 (5.98)	1.69	0.84	2.15	1.60	Rh	(16.59)	(...)	(6.80)	2.09	1.08	2.80	
								Pd	(17.96)	(...)	(6.80)	2.19	1.14	2.96	
Mo	7.69 (12.79)	0.69 (...)	4.57 (5.98)	1.79	0.90	2.31	2.52								

[a] For the excited configuration d^nsp, computed from SCF data of Fraga, Saxena, and Karwowski.[48] For the ground state, taken from SCF data of Fraga, Karwowski, and Saxena.[49] [b] Weighted average; computed from spectroscopic data given by Moore.[42] [c] Reference 47; ref 38, p 110. [d] For Sc, Ti, V, and Cr, see ref 44 and 29. For the rest, see ref 28. [e] Y. K. Syrkin and M. E Dyatkina "Structure of Molecules and the Chemical Bond", Dover Publications, New York, 1964, Chapter 14.

Table VI. Ground-State Electronic Configuration and Molecular Orbital Energies (eV) of the Repeating Unit $-M_2-$ for First-Series Transition Metals[a]

									Coulomb integrals for $d^n sp$ config of parent atomic orbital		
$-M_2-$	R, Å	$\sigma_g 3d$	$\pi_u 3d$	$\delta_g 3d$	$\delta_u 3d$	$\pi_g 3d$	$\sigma_u 3d$	$\sigma_u 3d + (\sigma_g 3d)^2$	H_{dd}	H_{ss}	H_{pp}
$-SC_2-$	2.878 (R_1)	$(-7.07)^2$	$(-6.87)^2$	$(-6.75)^0$				$(-7.07)^2$	−6.73	−2.08	−5.31
	2.30 (R_3	$(-7.36)^2$	$(-7.19)^2$	$(-6.82)^0$				$(-7.36)^2$			
$-Ti_2-$	2.648 (R_1)	$(-8.06)^2$	$(-7.88)^4$	$(-7.75)^0$				$(-8.06)^2$	−7.73	−2.07	−5.52
	2.50 (R_2)	$(-8.13)^2$	$(-7.95)^4$	$(-7.76)^0$				$(-8.13)^2$			
	2.30 (R_3)	$(-8.28)^2$	$(-8.07)^4$	$(-7.79)^0$				$(-8.28)^2$			
$-V_2-$	2.448 (R_1)	$(-8.80)^2$	$(-8.62)^4$	$(-8.49)^2$	$(-8.45)^0$			$(-8.80)^2$	−8.47	−1.95	−5.71
	2.35 (R_2)	$(-8.87)^2$	$(-8.67)^4$	$(-8.50)^2$	$(-8.44)^0$			$(-8.87)^2$			
	2.20 (R_3)	$(-8.98)^2$	$(-8.77)^4$	$(-8.52)^2$	$(-8.42)^0$			$(-8.98)^2$			
$-Cr_2-$	2.372 (R_1)	$(-9.56)^2$	$(-9.41)^4$	$(-9.31)^4$	$(-9.27)^0$			$(-9.56)^2$	−9.29	−1.82	−5.78
	2.34 (R_2)	$(-9.58)^2$	$(-9.42)^4$	$(-9.31)^4$	$(-9.27)^0$			$(-9.58)^2$			
	1.97 (R_3)	$(-9.89)^2$	$(-9.66)^4$	$(-9.35)^4$	$(-9.23)^0$			$(-9.89)^2$			
$-Mn_2-$	2.356 (R_1)	$(-10.27)^2$	$(-10.16)^4$	$(-10.09)^4$	$(-10.07)^2$			$(-10.27)^2$	−10.08	−1.63	−5.90
	2.25 (R_3)	$(-10.34)^2$	$(-10.18)^4$	$(-10.09)^4$	$(-10.06)^2$			$(-10.34)^2$			
$-Fe_2-$	2.340	$(-11.10)^2$	$(-11.03)^4$	$(-10.99)^4$	$(-10.97)^4$	$(10.93)^0$		$(-11.10)^2$	−10.98	−1.68	−6.20
$-Co_2-$	2.324	$(-11.63)^2$	$(-11.58)^4$	$(-11.55)^4$	$(-11.55)^4$	$(-11.52)^2$	$(-11.46)^0$	$(-11.63)^2$	−11.55	−1.54	−6.36
$-Ni_2-$	2.308	$(-12.18)^2$	$(-12.14)^4$	$(-12.13)^4$	$(-12.13)^4$	$(-12.12)^4$	$(-12.07)^0$	$(-12.18)^2$	−12.13	−1.28	−6.28

[a] Occupation numbers are given as superscripts.

Table VII. Ground-State Electronic Configuration and Molecular Orbital Energies (eV) of the Repeating Unit $-M_2-$ for Second-Series Transition Metals[a]

								Coulomb integrals for $d^n sp$ config of parent atomic orbital		
$-M_2-$	R, Å	$\sigma_g 4d$	$\pi_u 4d$	$\delta_g 4d$	$\delta_u 4d$	$\pi_g 4d$	$(\sigma_g 4d)^2$	H_{dd}	H_{ss}	H_{pp}
$-Y_2-$	3.232	$(-4.09)^2$	$(-4.09)^2$	$(-3.87)^0$			$(-4.09)^2$	−3.82	−1.16	−4.09
$-Zr_2-$	2.908 (R_1)	$(-5.61)^2$	$(-5.37)^4$	$(-5.06)^0$			$(-5.61)^2$	−4.98	−1.03	−4.26
	2.74 (R_2)	$(-5.66)^2$	$(-5.47)^4$	$(-5.09)^0$			$(-5.66)^2$			
$-Nb_2-$	2.684 (R_1)	$(-6.82)^2$	$(-6.61)^4$	$(-6.23)^2$	$(-6.03)^0$		$(-6.82)^2$	−6.13	−0.86	−4.23
	2.56 (R_2)	$(-6.83)^2$	$(-6.71)^4$	$(-6.26)^2$	$(-5.99)^0$		$(-6.83)^2$			
	2.30 (R_3)	$(-6.87)^2$	$(-6.94)^4$	$(-6.36)^2$	$(-5.88)^0$		$(-6.87)^2$			
$-Mo_2-$	2.592 (R_1)	$(-8.42)^2$	$(-8.20)^4$	$(-7.79)^4$	$(-7.59)^0$		$(-8.42)^2$	−7.69	−0.69	−4.57
	2.46 (R_2)	$(-8.50)^2$	$(-8.33)^4$	$(-7.82)^4$	$(-7.55)^0$		$(-8.50)^2$			
	2.07 (R_3)	$(-8.60)^2$	$(-8.79)^4$	$(-8.02)^4$	$(-7.31)^0$		$(-8.60)^2$			
$-Tc_2-$	2.542 (R_1)	$(-9.84)^2$	$(-9.55)^4$	$(-9.16)^4$	$(-9.00)^2$	$(-8.53)^0$	$(-9.84)^2$	−9.08	−0.81	−4.69
	2.12 (R_3)	$(-10.13)^2$	$(-10.09)^4$	$(-9.33)^4$	$(-8.81)^2$	$(-7.64)^0$	$(-10.13)^2$			
$-Ru_2-$	2.492 (R_1)	$(-10.94)^2$	$(-10.62)^4$	$(-10.26)^4$	$(-10.14)^4$	$(-9.73)^0$	$(-10.94)^2$	−10.20	−0.77	−4.97
	2.25 (R_3)	$(-11.18)^2$	$(-10.91)^4$	$(-10.33)^4$	$(-10.06)^4$	$(-9.33)^0$	$(-11.18)^2$			

[a] Occupation numbers are given as superscripts.

the metal atom to a configuration favorable to linear digonal bonding. To find the stabilization with respect to the normal ground state, which is more comparable with the bond dissociation energy, we must correct this ΔE^* by the configuration energy:

$$E(\text{bonding stabilization}) = E(-M_2-) - 2E(M^0\ d^n s^2 \text{ or } d^{n+1}s) = \Delta E^*(\text{bonding stabilization}) + 2[E(M^*\ d^n sp) - E(M^0\ d^n s^2 \text{ or } d^{n+1}s)] \quad (8)$$

A negative value means that the stabilization more than compensates for the energy expenditure of excitation.

There is also one important departure from a conventional molecular orbital study of diatomic systems. Because we purport to study one repeating unit in an infinite chain, the symbol $-(M_2)-$ indicates that we must save two electrons for digonal σ bonding to the two neighbors of this unit. Since the lowest energy orbital between two neighboring metal atoms is the dσ orbital, these two electrons naturally will seek out such an orbital for σ bonding. Therefore, in the total stabilization energy we must include the two electrons in this orbital in addition to the other bonding electrons within the diatomic metal system.

Table VIII. Energy (eV) and Other Data for the $d^n sp$ Configuration of Third-Series Transition Metals (Ground-State Values in Parentheses)

	VOIE (this work[a])						$d^n sp$ energy (this work[b])
	5d	6p	6s	ζ_{6s}	ζ_{6p}	ζ_{5d}	
La	(...)	(...)	(4.35)	1.525	0.700	1.66	2.08
Hf	(8.71)	(...)	(5.71)	3.068	2.383	4.03	3.25
Ta	(9.79)	(...)	(5.98)	3.091	2.433	4.16	3.88
W	(12.24)	(...)	(5.98)	3.175	2.483	4.29	3.34
Re	(13.87)	(...)	(6.26)	3.258	2.533	4.42	4.49
Os	(14.69)	(...)	(6.53)	3.341	2.583	4.55	3.23
Ir	(15.51)	(...)	(6.80)	3.425	2.633	4.68	4.19
Pt	(16.87)	(...)	(6.80)	3.508	2.683	4.81	5.32

[a] From the data of Fraga et al.[49] [b] Weighted average computed from spectroscopic data given by Moore.[42]

As an illustration, consider the $-(V_2)-$ unit, which consists of two $V(3d^3 4s4p)$ atoms. The lowest molecular orbitals with their energies and occupations are

$$\underset{-8.80\ \text{eV}}{(\sigma_g 3d)^2} \quad \underset{-8.62\ \text{eV}}{(\pi_u 3d)^4} \quad \underset{-8.49\ \text{eV}}{(\delta_g 3d)^2} \quad + \quad \underset{-8.80\ \text{eV}}{(\sigma_g 3d)^2} \qquad (9)$$

where the total of ten electrons are distributed among two groups: eight for bonding between the two V's and two for bonding to neighboring V's. The latter are also in σ_g3d orbitals

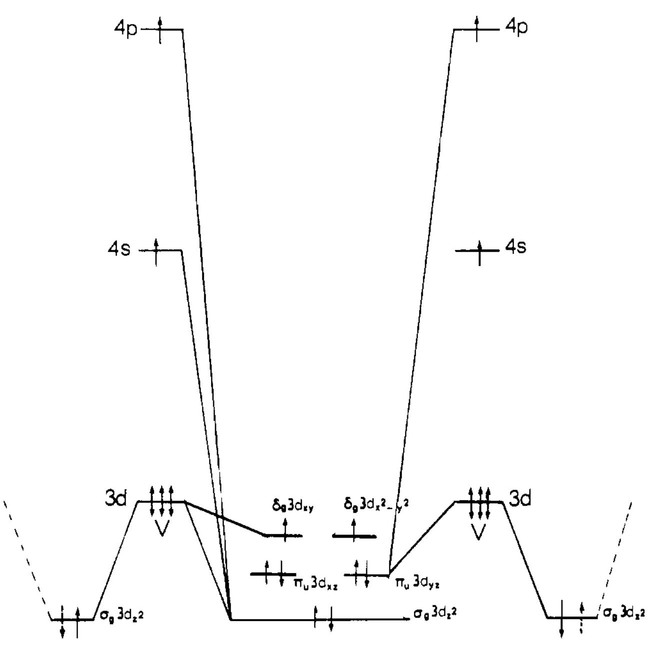

Figure 1. Valence bond and molecular orbital representation of the repeating unit $-V_2-$. Dotted lines indicate the electrons and the elements of the left and right nearest neighbors. Note that a total of two electrons, one on each side of the unit, are reserved for bonding with the two nearest neighbors.

(albeit the $\sigma_g 3d$ formed with neighboring atoms[52]). The ground configuration for all of the $-(M_2)-$ systems calculated are given in Tables VI and VII. For a normal V_2 diatomic molecule, the configuration would have been $(\sigma_g 3d)^2(\pi_u 3d)^4(\delta_g 3d)^4$ with a bond order of $n = 5$. Here, in in (9), the maximum bond order between the two vanadium atoms is $n = 4$. This kind of bonding picture is illustrated in Figure 1. Therefore, the total stabilization energy in (9), computed from eq 7 and 8, contains two π bonds, two δ bonds, and two σ bonds; viz., for $-(V_2)-$

$$\Delta E(\text{bonding stabilization}) = 2E(d\sigma) + 2E(d\pi) + 2E(d\delta) \qquad (10)$$

To delineate the contribution from different bond types, we must know the relative sizes of these bond energies. To get an estimate of the relative bond stabilization energy, we subtract the parent d-orbital VOIE (which is set to be the Coulomb integral H_{dd}) from the d-bonding molecular orbital and take the ratio

$$d\sigma:d\pi:d\delta = (\epsilon_{\sigma_g 3d} - H_{dd}):(\epsilon_{\pi_u 3d} - H_{dd}):(\epsilon_{\delta_g 3d} - H_{dd}) \qquad (11)$$

This ratio for $-(V_2)-$ is 1:0.454:0.0606. This is a much more realistic ratio than the simple ratio of d-orbital overlap, viz., $S(d\sigma,d\sigma):S(d\pi,d\pi):S(d\delta,d\delta)$, which is 1:0.461:0.0576. This is because in eq 11 the molecular orbital energies would have received input from the legitimately existing sσ, pσ, and pπ contributions and received modulation of the d bonding through mixing. Substitution of the ratio of eq 11 into eq 10 yields the bond energies $E(d\sigma)$, $E(d\pi)$, and $E(d\delta)$. $E(d\sigma)$ (=1.80 eV for the vanadium chain) is the single-bond energy to the neighbors, which is the minimum (σ-bond) stabilization energy between two metal atoms in a chain. For $-(V_2)-$ the maximum stabilization would come from the maximum bond order of 4 ($\sigma + 2\pi + \delta$) between the two V atoms. The average stabilization energy is for multiple bonds spread out by resonance conjugation along the chain, giving an average of one σ, one π, and a half δ bond between any two vanadium atoms. This average stabilization energy is computed to be 2.68 eV. This is really not comparable with the usual diatomic V_2 molecule, but for lack of other experimental data for comparison, we cite the bond dissociation energy[36] given for V_2, 2.46 eV. The agreement is fortuitous in view of the drastic approximation that we made. We think that the bonding in a chain should be much stronger because electron repulsion is reduced by digonal hybridization and by excitation to the d^{n}sp configuration. This stabilization should be further enhanced by resonance conjugation over an infinite chain, which is not possible in a di- or trinuclear complex. The presence of multiple bonds increases the possibility of conjugated resonance structures as illustrated by Figure 2. In resonance structures, we must distinguish the two π (i.e., π_x and π_y) and the two δ orbitals so that Pauli's exclusion principle is not violated in these conjugate structures. Similar structures may be drawn for other metals.[53] The data analyses discussed here are summarized in Tables IX and X. The application of the

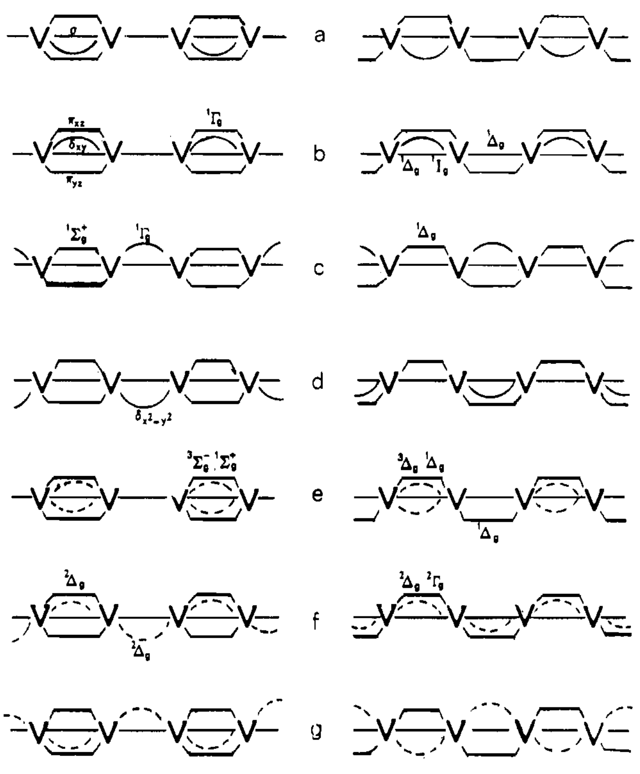

Figure 2. Multiple-bond configuration and resonance structure of the $(-V_2-)_n$ chain. A straight line is used to indicate the σ bond, a bracket to indicate the π bond, and a curve (chord) to indicate the δ bond. Translational symmetry for $-V_2-$ as a unit is preserved in all parts of the figure. Resonance structures requiring three or more V atoms as a repeating unit are not shown, although they may be important in unit cells with three or more atomic units. Coordinated resonance movement of bonds of the same type along either direction will not change the conjugation or the translational symmetry. However, if electronic angular momentum is to be conserved, only resonance structures with *common* angular momentum can interconvert to each other. Thus, the structures in parts a–d can interconvert but cannot transmute to those in parts e–g. The angular momentum for the diatomic unit and the three lowest resultant angular momenta of the chain are given for the resonance structures.

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(52) Normally for a diatomic molecule (rather than a diatomic unit in a chain), the two lone electrons relegated along the σ direction would have to be assigned to $\sigma_u 3d$ (−8.15 eV) or $\sigma_g 4s$ (−6.74 eV) to avoid violating Pauli's exclusion principle. But here the additional $\sigma_g 3d$ orbital may be visualized as the second molecular orbital between four atoms $-V^a-V^b-V^c-V^d-$; i.e., $\Psi_2 \simeq (d_\sigma^a + d_\sigma^b) - (d_\sigma^c + d_\sigma^d)$, which is bonding between ab and between cd and which, in a chain with a dσ band is only very slightly higher than the lowest molecular orbital $\Psi_1 \simeq d_\sigma^a + d_\sigma^b + d_\sigma^c + d_\sigma^d$. The difference in energy between two successive orbitals in a $2N$ atomic chain is $2\beta \cos [(k + 1)\pi/(N + 1)] - 2\beta \cos [k\pi/(2N + 1)]$, with N approaching infinity and k ranging from 1 to $2N$.

(53) Y. N. Chiu and F. E. Wang, *J. Solid State Chem.*, in press.

Table IX. Bonding Stabilization in a Linear Chain of First-Series Transition-Metal Atoms (in eV)[a]

confign energy	4.23	5.77	7.58	0.49	12.93	10.88	10.11	9.32	
M*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
$3d^n4s4p$	dsp	d^2sp	d^3sp	d^4sp	d^5sp	d^6sp	d^7sp	d^8sp	
bonding stabilizn, $E(-M_2-) - 2E(M^* d^n sp)$	−13.78	−17.66	−20.52	−23.60	−26.36	−28.84	−30.78	−33.60	R_1
		−18.22	−21.02	−23.72					R_2
	−15.58	− 19.30	−21.90	−26.08	−26.70				R_3
$E(-M_2-) - 2E(M^0 \text{ ground})$	−5.32	−6.12	−5.36	−22.62	−0.50	−7.08	−10.56	−14.96	R_1
		−6.68	−5.86	−22.74					R_2
	−7.12	−7.76	−6.74	−25.10	−0.84				R_3
max ΔE for $M\overset{n}{-}M$ bond in chain	−3.11	−4.01	−3.55	−15.17	−0.327	−4.58	−6.11	−7.48	R_1
		−4.52	−3.95	−15.24					R_2
	−4.51	−5.36	−4.68	−17.79	−0.541				R_3
max bond order in chain (n)	2 (σ,π)	3 (σ,2π)	4 (σ,2π,δ)	5 (σ,2π,2δ)	4 (σ,2π,δ)	3 (σ,2π)	2 (σ,π)	1 (σ)	
av ΔE for M–M in chain	−2.66 (σ,π/2)	−3.05 (σ,π)	−2.68 (σ,π,δ/2)	−11.31 (σ,π,δ)	−0.25 (σ,π,δ/2)	−3.54 (σ,π)	−5.28 (σ,π/2)	−7.48 (σ)	R_1
		−3.34 (σ,π)	−2.93 (σ,π,δ/2)	−11.37 (σ,π,δ)					R_2
	−3.56 (σ,π/2)	−3.88 (σ,π)	−3.37 (σ,π,δ/2)	−12.55 (σ,π,δ)	−0.42 (σ,π,δ/2)				R_3
min estd σ-bond ΔE in chain	−2.21 (σ)	−2.10 (σ)	−1.80 (σ)	−7.45 (σ)	−0.17 (σ)	−2.49 (σ)	−4.44 (σ)	−7.48 (σ)	R_1
		−2.11 (σ)	−1.90 (σ)	−7.49 (σ)					R_2
	−2.61 (σ)	−2.39 (σ)	−2.06 (σ)	−7.31 (σ)	−0.29 (σ)				R_3
rel stabilizn (dσ = 100), dπ:dδ	41:5.8	45:6.0	45:6.0	44:7.4	42:5.2	41:8.3	37:0	20:0	R_1
		55:7.5	50:7.5	44:6.9					R_2
	73:14.3	62:10.9	58:9.8	61:10	38:3.8				R_3
exptl stabilizn,[b] $D_0^\circ(M^\circ_2)$	−1.65 ± 0.22	−1.30 ± 0.17	−2.46 ± 0.22	−1.56 ± 0.22	−0.43 ± 0.30	−1.03 ± 0.22	−1.73 ± 0.26	−2.38 0.22	

[a] Values of R_1, R_2, and R_3 are given in Table I. [b] J. A. Connor and H. A. Skinner in "Reactivity of Metal–Metal Bonds", ACS Symp. Ser. No. 155, M. H. Chisholm, Ed., American Chemical Society, Washington, DC, 1981, pp 197–205.

Table X. Bonding Stabilization in a Linear Chain of Second-Series Transition-Metal Atoms (in eV)[a]

confign energy	5.72	7.03	1.60	2.52	12.24	0.82	
M*	Y	Zr	Nb	Mo	Tc	Ru	
$4d^n5s5p$	dsp	d^2sp	d^3sp	d^4sp	d^5sp	d^6sp	
bonding stabilizn, $E(-M_2-) - 2E(M^* d^n sp)$	−6.40	−13.42	−19.22	−25.60	−30.40	−33.96	R_1
		−14.02	−19.72	−26.56			R_2
			−21.00	−29.60	−34.02	−36.04	R_3
$E(-M_2-) - 2E(M^0 \text{ ground})$	+5.04	0.64	−16.02	−20.56	−5.92	−32.32	R_1
		0.04	−16.52	−21.52			R_2
			−17.80	−24.56	−9.54	−34.40	R_3
max ΔE for $M\overset{n}{-}M$ bond in chain	3.36	0.442	−11.49	−14.96	−4.15	−22.01	R_1
		0.028	−12.22	−16.00			R_2
			−13.84	−19.78	−7.25	−24.42	R_3
max bond order in chain (n)	2 (σ,π)	3 (σ,2π)	4 (σ,2π,δ)	5 (σ,2π,2δ)	4 (σ,2π,δ)	3 (σ,2π)	
av ΔE for M–M in chain	2.52 (σ,π/2)	0.320 (σ,π)	−8.01 (σ,π,δ/2)	−10.28 (σ,π,δ)	−2.96 (σ,π,δ/2)	−16.16 (σ,π)	R_1
		0.020 (σ,π)	−8.26 (σ,π,δ/2)	−10.76 (σ,π,δ)			R_2
			−8.90 (σ,π,δ/2)	−12.28 (σ,π,δ)	−4.77 (σ,π,δ/2)	−17.20 (σ,π)	R_3
min estd σ-bond ΔE in chain	1.68 (σ)	0.197 (σ)	−4.53 (σ)	−5.60 (σ)	−1.77 (σ)	−10.31 (σ)	R_1
		0.011 (σ)	−4.29 (σ)	−5.51 (σ)			R_2
			−3.95 (σ)	−4.77 (σ)	−2.29 (σ)	−9.97 (σ)	R_3
rel stabilizn (dσ = 1), dπ:dδ	1.00:0.185	0.619:0.127	0.695:0.145	0.698:0.137	0.618:0.105	0.567:0.081	R_1
		0.720:0.162	0.828:0.186	0.790:0.160			R_2
			1.09:0.311	1.21:0.362	0.962:0.238	0.724:0.132	R_3
exptl stabilizn, $D_0^\circ(M^\circ_2)$	−1.61 ± 0.22		−5.21 ± 0.10	−4.19 ± 0.20			

[a] Values of R_1, R_2, and R_3 are given in Table II. [b] J. A. Connor and H. A. Skinner in "Reactivity of Metal–Metal Bonds", ACS Symp. Ser. No. 155, M. H. Chisholm, Ed., American Chemical Society, Washington, DC, 1981, pp 197–205. For triple-bonded Mo≡Mo in Mo_2X_6 complexes the bond energy was estimated[11] to be 5.46 ± 0.65 kcal' Our relative stabilization ratios give δ-bond energy of 17.7 kcal for $-Mo_2-$ and 4.3 kcal for $-Tc_2-$ compared with the upper limits of the σ-bond energy of 20–18 kcal estimated by Trogler and Gray.[4]

multiple-bonding concept to superconductivity in A_3B (A15 type) alloys is discussed in a separate paper.[53] If we take the stabilization of the d orbital (relative to the VOIE of d) due to π or δ interaction as β (i.e., let $\epsilon_{\pi,3d} - H_{dd} = \beta_\pi$ and $\epsilon_{\delta,3d} - H_{dd} = \beta_\delta$), then in a chain of $2N$ metal atoms the stabilization energy of the π molecular orbitals[54] becomes $2\beta_\pi \cos [k\pi/(2N + 1)]$ ($k = 1, 2, 3, ..., 2N - 1$), instead of β_π. If each metal atom has a π electron, the total of $2N$ electrons will occupy doubly in a ground state, up to the $K = N$ molecular orbital.

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(54) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966.

For large values of N, the average energy of a π electron, which previously was β_π, becomes

$$\lim_{N\to\infty} [2\sum_{k=1}^{N} 2\beta_\pi \cos [k\pi/(2N+1)]](2N)^{-1} = 4\beta_\pi[\lim_{N\to\infty} (1/\pi)][(2N+1)/2N] \int_{\pi/(N+1)}^{N\pi/(2N+1)} \cos x \, dx = 4\beta_\pi/\pi \simeq 1.27\beta_\pi \quad (12)$$

The 0.27 or 27% is the resonance energy gain for each π (or δ) electron upon formation of an infinite chain. This 27% may also be used as a rough estimate of the bond stabilization gain due to resonance conjugation upon formation of an infinite chain.

Discussion

It should be reiterated that the change overlaps that we obtained are based on rather primitive single-ζ Slater orbitals. This was done in the interest of internal self-consistency (among and between different transition series) in making comparisons. Although other ζ values are available[55] and some double-ζ functions etc. are also known, none cover the whole range of the three transition series. It should perhaps also be mentioned that these single-ζ Slater orbitals have been recently used[28,29,44] for diatomic metal molecules M_2 with reasonable results. However, strictly speaking, our results for the repeat unit, $-(M_2)-$ in a chain, should not be compared with diatomic M_2 or with the M–M bonding in complexes. The agreement of the δ-bond energy for Mo of 17.7 kcal computed here (Table X) with the 17–20 kcal estimated by Trogler and Gray for complexes[4] as well as the agreement of the average stabilization energy of $-(V_2)-$ of 2.68 eV (Table IX) with the experimental value[36] of 2.46 eV is to be considered as accidental, although it might serve to show that our values are not too far out of line. The same may be said of our use of the same parameter $K = 1.75$ to approximate the known dissociation energies of N_2 and P_2 (Table IV).

It should be noted that the lowest bonding orbitals are called σnd, πnd, and δnd because they are derived mainly from the lower energy (low H_{DD}) d orbitals, which contributed larger coefficients in MO. But, because of the larger overlaps of s and p orbitals (see below), the bonding strength may be considered to come mainly from s (as if through sp and then dp hybrid) and p orbitals (as if through dp hybrid).

Although we make no pretense of rigor, from comparison of the overlaps between different series, several trends appear.

For the same type of overlaps generally

$$S(5s,5s) > S(4s,4s) >> S(6s,6s)$$
$$|S(6p_\sigma,6p_\sigma)| >> |S(5p_\sigma,5p_\sigma)| > |S(4p_\sigma,4p_\sigma)|$$
$$S(5p_\pi,5p_\pi) > S(4p_\pi,4p_\pi) >> S(6p_\pi,6p_\pi)$$
$$S(4d_\sigma,4d_\sigma) > S(3d_\sigma,3d_\sigma) > S(5d_\sigma,5d_\sigma)$$
$$S(4d_\pi,4d_\pi) > S(3d_\pi,3d_\pi) > S(5d_\pi,5d_\pi)$$
$$S(4d_\delta,4d_\delta) > S(3d_\delta,3d_\delta) > S(5d_\delta,5d_\delta)$$

Because of the generally larger 4d overlap (compared with 3d and 5d), it would seen that multiple d bonding should be stronger when bonding occurs in the second transition series (to be followed by the first and then the third series). This is confirmed by the calculated stabilization energies (Tables IX and X). Although molecular orbital calculations were not carried out for the third series, it is noted that the overlaps are comparable (Table III) and the excitation energies to the digonal hybrid d^{n}sp are also not prohibitively large (Table VIII). Experimentally, multiple-bonded complexes of the third series such as Ta, W, and Re are, of course, well-known. In particular, the large size of the 6p$_\sigma$ overlap would suggest a stronger σ (relative to π and δ) bond. In fact, the larger sizes (especially for the third and to a larger extent for the second series) of the p overlaps are suprising. This, coupled with the relatively large size of the s overlap (and the (S,D), (P,D) and (SP) overlaps), then suggests a dp digonal hybridization. This is supported by the coefficients in the MO eigenfunctions. The relative size of the different overlaps within the same series are generally as follows:

first series:

$$S(4p_\pi,4p_\pi) \simeq S(4s,4p_\sigma) > S(4s,4s) > |S(4p_\sigma,4p_\sigma)| > S(4s,3d_\sigma) \simeq S(3d_\sigma,3d_\sigma) > S(4p_\pi,3d_\pi) \simeq S(3d_\pi,3d_\pi) > |S(4p_\sigma,3d_\sigma)| > S(3d_\delta,3d_\delta)$$

second series:

$$S(5p_\pi,5p_\pi) \simeq S(5s,5p_\sigma) > S(5s,5s) > |S(5p_\sigma,5p_\sigma)| > S(4d_\sigma,4d_\sigma) > S(5s,4d_\sigma) \simeq S(4d_\pi,4d_\pi) > S(5p_\pi,4d_\pi) > |S(5p_\sigma,4d_\sigma)| > S(4d_\delta,4d_\delta)$$

third series:

$$S(6p_\sigma,6p_\sigma) > S(6s,6p_\sigma) > S(6p_\pi,6p_\pi) > S(6s,6s) > S(6p_\sigma,5d_\sigma) > S(6s,5d_\sigma) > S(6p_\pi,5d_\pi) \simeq S(5d_\sigma,5d_\sigma) > |S(5d_\pi,5d_\pi)| \simeq |S(5d_\delta,5d_\delta)|$$

The generally small d overlaps show that mixing with the relatively larger s,p overlaps must be considered. The generally large p$_\pi$ overlap shows the importance of its effect on π bonding in d orbitals through mixing. In the third series there is, however, a reversal of the relative sizes of p$_\pi$ and p$_\sigma$ overlap—showing that 6p overlap, which is larger, must feature prominently in the σ bonding in dp digonal hybridization for a linear chain. The stabilization energy for both the first and second series shows a slow rise from group 3, reaching a maximum in group 6 (Cr and Mo) with a sudden dip in the first column of group 7 (Mn and Tc) followed by a rise in other columns of groups 7 and 8. In series 2 the stabilization energies for the first two elements, Y and Zr, are positive, corresponding to destabilization. However, a stable Y_2 molecule is known. Instead of attributing this to the inadequacy of our method, we would like to submit that, inasmuch as we impose a d^{n}sp configuration for digonal bonding for all, it just means that Y and Zr are relatively unstable with respect to the formation of a bare linear chain. And, as a result, other stabilization factors (e.g., ligands or neighboring groups), other interactions, or other hybrid schemes[59] may be needed in a crystal with identifiable linear chains of such atoms as Y and Zr. We used three sets of interatomic distances: R_1 computed from Pauling's[60] metallic radii, a shorter R_2 from interatomic distances between A atoms found in A_3B (A15-type) compounds, and the shortest R_3 from interatomic distances of known multiple bonds (between V, Cr, Mo, Tc, and W). We also put in a few extrapolated short distances in other metals that would apply if multiple bonds were to form in such metals (Sc, Ti, Mn, Nb, Ta). All these short distances turn out to have favorable stabilization energy. The stabilization energy for the range of R's studied generally increases with decrease in R. From the gradual rate of increase it seems that, given the known multiple bonds in R_3, which does not show an abrupt and unique change in energy, there is the possibility of multiple-bond stabilization in R_2 (for the A_3B compounds). For a linear chain, our analysis shows that, because of the need to reserve electrons to bond the neighbors on two sides (for

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(56) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177–478 (1974).

(57) A. D. McLean, Report, IBM Research Laboratory, San Jose, CA, 1980.

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(59) E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure", 4th ed., Butterworths, London, 1977, p 128.

(60) L. Pauling, "The Nature of the Chemical Bonds", 3rd ed., Cornell University Press, Ithaca, NY, 1960.

chain extension), the bond orders for $-(M_2)-$ are generally 1 order less than those (Tables IX and X) of M_2. In spite of our apologies for the crudeness of our calculations, we feel that the comparative study is valid. The Appendix gives the reason that the use of overlap to approximate bonding stabilization is valid and also shows that the omitted terms tend to cancel.

Finally, our neglect of f orbitals is justified, not only because they do not occur in the excited configuration as open shell except in La atoms but also because, even in this case, the f overlaps are computed to be small, viz. (for 5d6s4f configuration)

$$S(6s,4f_\sigma) = 0.002$$
$$S(5d_\sigma,4f_\sigma) = 0.008$$
$$S(4f_\sigma,4f_\sigma) = 0.000$$

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Appendix. Theoretical Estimate of Bond Strength

The rigorous definition of equilibrium bond dissociation is straightforward, being just the energy difference between the molecule and the atoms it dissociates into. In a homonuclear diatomic molecule A_2, it is

$$D_e = 2E(A) - E(A_2) \tag{A-1}$$

The attempts to calculate rigorously the bond dissociation energy for many-electron diatomic molecules, however, are not always satisfactory. For example, the extended-basis SCF–LCAO–MO calculations[61–63] for N_2 yielded a D_e of 5.27 eV vs. an experimental value of 9.76 eV.

The attempts to theorectically estimate bond dissocation energy are frequently devious and confusing, in some cases because of the use of electronic energies without explicit reference as to how the nuclear repulsion was taken into account and in other cases because of the use of one-electron energies without regard for correlation and two-electron Coulomb and exchange energies. For example, Mulliken and Ermler[64] estimate the bond strength to be

$$D_e = C\eta\bar{I} \tag{A-2}$$

where C is constant, η is the charge overlap, and $\bar{I}$ is the average ionization potential of the atoms. Simple molecular orbital theory approximates the dissociation energy in terms of the resonance integral β. For example,[65] for the C_2 molecule with a $(\pi_u 2p)^4$ configuration (occupation number $N = 4$, $\beta = \beta_{2\pi}$)

$$D_e = -\sum_i N_i\beta_i = -4\beta_{2p\pi} \tag{A-3}$$

Bond dissociation energy has also be defined[66] in terms of atomic ionization potential (I) and atomic electron affinity (E_A) and a modified resonance integral β in the Wolfberg–Helmholz[37] extended[27] Hückel approximation as follows (for a homonuclear diatomic molecule):

$$D_e = -I + E_A - 2\beta' \tag{A-4}$$

where $\beta' = (K - 1)SH_{aa}/(1 + S)$ with K a constant, S the overlap integral, and H_{aa} the Coulomb integral equal to $\int \Phi_a(i)\cdot H_i\Phi_a(i)\,d\tau_i$. Other more sophisticated elaborations of the above approximations are available.[46,67] The fact that these approximations apparently work fairly well, given the diversity of approach and the vagaries of approximations, calls for an explanation.

It is the purpose of this appendix to delineate the quantum-mechanical basis for the approximations and assumptions used in the present work and to show their relationship to the few existing approximations. We use a simplified case to illustrate the theoretical principles involved. Consider two identical atoms a and b, each with a hypothetical doubly positively charged atomic core ($Z = 2$) plus two electrons in the sp configuration (and in the triplet state for better illustration). The Hamiltonian for atom a is

$$H_a = \frac{1}{2}\nabla_1{}^2 - \frac{1}{2}\nabla_2{}^2 - \frac{Z}{r_{1a}} - \frac{Z}{r_{2a}} + \frac{Z}{r_{12}} \tag{A-5}$$

which has a single-configuration self-consistent field (SCF) solution $\psi_a = |S_a(1)\ P_{\pi a}(2)|$ with SCF energy

$$E_a(A) = E(A) = \epsilon_s + \epsilon_p + J_{sp} - K_{sp} \tag{A-6}$$

The SCF orbital energies are identifiable with ionization potentials (or VOIE's, valence-orbital ionization energies) by Koopmans theorem; i.e., $\epsilon_s \simeq -I_s$ and $\epsilon_p \simeq -I_p$ and the Coulomb (J) and exchange (K) integrals are defined as

$$J_{sp} = \int \frac{S_a{}^2(1)\ P_{\pi a}{}^2(2)}{r_{12}}\,d\tau_{12} = (S_aS_a|P_{\pi a}P_{\pi a})$$

$$K_{sp} = \int \frac{S_a(1)\ P_{\pi a}(1)\ S_a(2)\ P_{\pi a}(2)}{r_{12}}\,d\tau_{12} = (S_aP_{\pi a}|S_aP_{\pi a}) \tag{A-7}$$

Similar expressions may be written for atom b. When a and b combine to form a diatomic molecule, the resulting Hamiltonian for the four electrons is

$$H = H_a + H_b + H^1 = H_a + H_b - \frac{Z}{r_{1b}} - \frac{Z}{r_{2b}} - \frac{Z}{r_{3a}} - \frac{Z}{r_{4a}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{Z^2}{R_{ab}} \tag{A-8}$$

The SCF single-configuration ground-singlet molecular-orbital wave function may be written as[68,69]

$$\psi = |\sigma_g(1)\ \bar{\sigma}_g(2)\ \pi_u(3)\ \bar{\pi}_u(4)| \tag{A-9}$$

The SCF energy for the molecule is

$$E^1(A_2) = 2\epsilon_\sigma + 2\epsilon_\pi + J_{\sigma\sigma} + J_{\pi\pi} + 4J_{\sigma\pi} - 2K_{\sigma\pi} \tag{A-10}$$

which traditionally contains electronic energy alone and excludes the nuclear repulsion energy Z^2/R_{ab}. The Coulomb (J) and exchange (K) integrals are defined similarly to those in (A-7), albeit by using molecular orbitals σ_g and π_u. The bond

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dissociation energy with nuclear repulsion included is then

$$D_e = 2E'(\mathrm{A}) - E(\mathrm{A}_2) - \frac{Z^2}{R_{ab}} = 2(\epsilon_s + \epsilon_p) - 2(\epsilon_\sigma + \epsilon_\pi) + [(J_{sp} - K_{sp}) - (J_{\sigma\sigma} + J_{\pi\pi} + 4J_{\sigma\pi} - 2K_{\sigma\pi})] - \frac{Z^2}{R_{ab}} \quad \text{(A-11)}$$

Approximation A-3 with one-electron resonance energy β is similar to the use of the first two terms alone. It represents reliance on one-electron energies to approximate D_e. Even if these are SCF energies, it still means the neglect for all two-electron Coulomb and exchange integrals, which must be assumed to either cancel or almost cancel. And, unless nuclear repulsion is already *included* in electron energies (which is almost never the case, except perhaps in the H_2^+ ion), account must be given of it. The use of electron overlap to approximate D_e such as in (A-1) and (A-4) also must account for the absence of the *nuclear* repulsion term. The questions are as follows: (1) Will the two electron integrals cancel? (2) Will the nuclear repulsion term be canceled? A typical two-electron molecular-orbital integral may be expanded into atomic orbital integrals as in

$$J_{\sigma\pi} = \frac{1}{2(1 + S_\sigma)(1 + S_\pi)}[(S_aS_a|P_{\pi a}P_{\pi a}) + 2(S_aS_a|P_{\pi a}P_{\pi b}) + (S_aS_a|P_{\pi b}P_{\pi b}) + (S_aS_b|P_{\pi a}P_{\pi a}) + 2(S_aS_b|P_{\pi a}P_{\pi b}) \quad \text{(A-12)}$$

It is expected that most of the *one-center* two-electron integrals (e.g., $(S_aS_a|P_{\pi a}P_{\pi a})$, which happen to be the largest, will cancel with the corresponding (one-center) atomic Coulomb and exchange integrals (eq A-6 and A-7). But it is necessary to assume that the two-center two-electron integrals must be small or otherwise fortuitously cancel. Actually they are not that small. Examples of the latter in case of the π system of ethylene are[68] $(P_{\pi a}P_{\pi b}|P_{\pi a}P_{\pi b}) = 1.08$ eV and $(P_{\pi a}P_{\pi a}|P_{\pi a}P_{\pi b}) = 3.57$ eV compared with the one-center integral $(P_{\pi a}P_{\pi a}|P_{\pi a}P_{\pi a}) = 16.92$ eV. Other examples are available.[70,71]

While all of the (neglected) two-center two-electron integrals will depend on the overlap to some extent (first or second order), energy is through the molecular orbital energy ϵ_σ and ϵ_π. For the ease of illustration, we use a simple (instead of SCF) Hamiltonian to compute the one-electron molecular orbital energy:

$$\begin{aligned} \epsilon_\pi &= \int \pi_u^*(1)\, H(1)\, \pi_u(1)\, d\tau_1 = \\ &\frac{1}{2(1 + S)}\int (P_{\pi a}(1) + P_{\pi b}(1))^* \left(-\frac{1}{2}\nabla_1{}^2 - \frac{Z}{r_{1a}} - \frac{Z}{r_{1b}}\right) \times (P_{\pi a}(1) = P_{\pi b}(1))\, d\tau_1 = \\ &\epsilon_p - \frac{1}{1 + S_\pi}\left[\left(P_{\pi a}(1)\left|\frac{Z}{r_{1b}}\right|P_{\pi a}(1)\right) + \left(P_{\pi a}(1)\left|\frac{Z}{r_{1b}}\right|P_{\pi b}(1)\right)\right] + \\ &\frac{1}{2(2 + S_\pi)}[H^P{}_{aa} + 2H^P{}_{ab} + 2H^P{}_{bb}] \quad \text{(A-13)} \end{aligned}$$

where

$$H^P{}_{aa} = \epsilon_p - \left(P_a(1)\left|\frac{Z}{r_{1b}}\right|P_a(1)\right) \quad \text{(A-14)}$$

$H_{pp} = \epsilon_p = -I_p = -P_\pi$ VOIE as the valence orbital ionization energy of the p_π atomic orbital, if we allow that H actually contains all of the electron interactions with the remaining electrons including the core. The term

$$\left(P_a(1)\left|\frac{Z}{r_{1b}}\right|P_a(1)\right)$$

is a Coulomb attraction term between electron number 1 and nuclear "b".

If we use the Mulliken–Wolfsberg–Helmholz approximation[37,38] for H_{ab} $(=KSH_{aa})$, eq A-13 becomes

$$\epsilon_\pi = \epsilon_p - \left(P_a(1)\left|\frac{Z}{r_{1b}}\right|P_a(1)\right) + \frac{(K - 1)S_\pi H^P{}_{aa}}{1 + S_\pi} = H^P{}_{aa} + \frac{(K - 1)S_\pi H^P{}_{aa}}{1 + S_\pi} \quad \text{(A-15)}$$

There will be a similar equation for ϵ_σ, which also has the term that represents the Coulomb attraction between electron number 1 on "a" with the nucleus at "b" i.e.

$$\left(S_a(1)\left|\frac{Z}{r_{1b}}\right|S_a(1)\right)$$

When ϵ_π and ϵ_σ are substituted into (A-11) to get bond dissociation energy, there will be four such terms if $Z = 2$ and nine such terms if $Z = 3$. If we take the classical picture, neglect the shielding by other electrons, and equate $r_{1b} = R_{ab}$, these then become the Coulomb repulsion term Z^2/R_{ab}—this is another way of saying that the two atoms as well as the molecule are neutral; i.e., the repulsion is neutralized (canceled).

If all of the above assumptions about Coulomb and exchange integrals are made and all of the approximations are accepted, then the bond dissociation energy becomes for the noninteracting σ and π electrons

$$D_e = -2\left[\frac{(K - 1)S_\pi H^P{}_{aa}}{1 + S_\pi} + \frac{(K - 1)S_\sigma H^S{}_{aa}}{1 + S_\sigma}\right] = -\Delta E(\text{bonding stabilization}) \simeq 2(H_{pp} + H_{ss}) - 2(\epsilon_\sigma + \epsilon_\pi) \quad \text{(A-16)}$$

This is the basic expression we use to estimate bonding strength. Elaboration will involve several σ or π orbitals interacting among themselves. Because of the nuclear repulsion and electron repulsions that have been underestimated (or neglected), the bond strength here is an overestimate. The proportionality to overlap integral in remarkable. It is perhaps precisely because the neglected two-center integrals are proportional to overlap that the bond energy is amenable to treatment using the parametric proportionality constant K. (Further refinements will involve proportionality to quadratic of overlap.) In fact, it is very sensitive to the choice of K, the constant in the Wolfsberg–Helmholz approximation. A change of K from 1.5 to 1.25 will reduce the D_e by about half. Although it is possible to adjust K to get agreement with experimental bond energy for carbon bonds and for nitrogen bonds, we choose not to. Instead, we use the same K for all. This is in part because the extent that we *overestimate* the bond energy for the first-row atoms (C and N) may be an indication of the extent of our *underestimation* of the bond energies for the second and third transition series. The value of $K = 1.5$ is in the lower range of the commonly used K's for transition metal heteropolar bonds.[38,45,47,72]

Registry No. Sc, 7440-20-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Y, 7440-65-5; Zr, 7440-67-7; Nb, 7440-03-1; Mo, 7439-98-7; Tc, 7440-26-8; Ru, 7440-18-8; Rh, 7440-16-6; Pd, 7440-05-3; La, 7439-91-0; Hf, 7440-58-6; Ta, 7440-25-7; W, 7440-33-7; Re, 7440-15-5; Os, 7440-04-2; Ir, 7439-88-5; Pt, 7440-06-4.

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