

SUPPORTING INFORMATION:

Distinguishing Bonds

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Table of Contents

Test of Reliability with Respect to the Level of Theory	1
Analysis of Some Homonuclear Diatomics	2
Q and Select Bond Characteristics For All Investigated Diatomics, Including Correlation Energy.	3
Tentative Relationship Between Q and Overlap of Atomic Orbitals	5
Comments on the Possibility of Scaled Measures of Covalency (0-100%)	6

Test of Reliability with Respect to the Level of Theory

TABLE S0. Reliability of ΔE , $\Delta\bar{\chi}$, $\Delta\omega$ and Q with respect to level of theory, tested on nitrogen oxide. The experimental bond length and the 6-31+G(d) basis set was used. All levels of theory agree on $\Delta\bar{\chi}$, but the missing correlation energy in Hartree-Fock (UHF) results in a too small bond energy, and a greatly overestimated Q.

² NO	ΔE	$\Delta E/n$	$\Delta\bar{\chi}$	$\Delta\omega/n$	$\Delta(V_{NN}+\omega)/n$	Q
Best Est. ^a	-6.66	-0.44	-2.08	-45.08	+1.64	8.4
ULC-BLYP	-6.81	-0.45	-2.11	-45.06	+1.65	8.3
UB3LYP	-6.53	-0.44	-2.12	-45.03	+1.68	8.7
UPBE	-7.28	-0.49	-2.07	-45.13	+1.58	7.5
U ω B97X-D	-6.48	-0.43	-2.16	-44.99	+1.73	9.0
UHF	-2.10	-0.14	-2.12	-44.74	+1.98	29.3

^a ΔE is experimental, $\Delta\bar{\chi}$ evaluated using ULC-BLYP/aug-cc-pVQZ

Analysis of Some Homonuclear Diatomics

TABLE S1. Bond character of homonuclear diatomics determined via an intermixed use of experimental and theoretical data.

Reaction ^a :	ΔE^b [eV]	$\Delta E/n$ [eV e ⁻¹]	$\Delta\bar{\chi}^c$ [eV e ⁻¹]	$\Delta(V_{\text{NN}} + \omega)/n$ [eV e ⁻¹]	Q
2 ² H → H ₂	-4.792	-2.396	-1.828 ^a	-0.568	0.53
2 ² Li → Li ₂	-1.09	-0.181	+0.54	-0.72	-6.9
2 Be → Be ₂	-0.11 ^d	-0.014	-0.10	+0.09	13.2
2 ² B → ³ B ₂	-3.07	-0.307	-0.59	+0.29	2.9
2 ³ C → C ₂	-6.29	-0.524	-1.08	+0.56	3.1
2 ⁴ N → N ₂	-9.94	-0.710	-2.35	+1.64	5.6
2 ³ O → ³ O ₂	-5.26	-0.329	-1.70	+1.37	9.3
2 ² F → F ₂	-1.70	-0.095	-0.80	+0.71	16.0
2 ² Na → Na ₂	-1.81	-0.035	+0.60	-0.63	-35.2
2 ² Al → ³ Al ₂	-1.81	-0.070	-0.09	+0.02	1.5
2 ² Cl → Cl ₂	-2.55	-0.075	-0.43	+0.35	10.4

^aThe spin multiplicity is singlet, unless otherwise specified. ^bExperimental data from NIST Chemistry WebBook. $\Delta E \approx \Delta H^0 - E_{\text{ZPE}}$, where $E_{\text{ZPE}} = \frac{1}{2}h\sum v_i$. ^cFrom LC-BLYP/aug-cc-pVQZ calculations, except for H and H₂, where the experimental values of $\bar{\chi}_{\text{H}} = -13.598$ eV and $\bar{\chi}_{\text{H}_2} = -15.426$ eV were used. ^d $\Delta E \approx \Delta H^0$ as E_{ZPE} can be presumed small, and no vibrational data is available for Be₂.

Q and Select Bond Characteristics For All Investigated Diatomics, Including Correlation Energy.

TABLE S2. A Q value deviating from unity implies the presence of multielectron effects. One part of such multielectron effects includes the missing post-Hartree-Fock correlation energy.

Species ^a	Q	ΔE^b	$\Delta\bar{\chi}^c$	$\Delta(V_{\text{NN}} + \omega)/n$	ΔE	Correlation energy ^d (%)
		Exp. (eV)	[eV e ⁻¹]	[eV e ⁻¹]	HF/aug-cc-pVQZ (eV)	
Ne ₂	~79	-364x10 ⁻⁵	-727x10 ⁻⁵	+708x10 ⁻⁵	+159x10 ^{-5f}	144
Kr ₂	~57	-173x10 ⁻⁴	-693x10 ⁻⁵	+669x10 ⁻⁵	+167x10 ^{-4f}	197
Xe ₂	~57	-243x10 ⁻⁴	-658x10 ⁻⁵	+635x10 ⁻⁵	+233x10 ^{-4f}	196
Ar ₂	~37	-123x10 ⁻⁴	-646x10 ⁻⁵	+611x10 ⁻⁵	+110x10 ^{-4f}	189
He ₂	~29	-944x10 ⁻⁶	-354x10 ⁻⁵	+330x10 ⁻⁵	-720x10 ^{-6f}	177
I ₂	24.8	-1.58	-0.19	+0.18	-0.65 ^f	59
F ₂	16.0	-1.70	-0.80	+0.71	+1.6	195
OF	14.2	-2.31	-1.03	+0.90	+0.7	129
Be ₂	13.2	-0.11 ^e	-0.10	+0.09	+0.3	384
ClF	13.0	-2.65	-0.71	+0.61	-0.3	87
NF	11.3	-3.21	-1.24	+1.04	-0.9	73
H ₂ ⁺	11.3	-2.65	-16.34	+13.688	-2.8	5
Cl ₂	10.4	-2.55	-0.43	+0.35	-0.8	69
O ₂	9.3	-5.26	-1.70	+1.37	-1.4	73
NO	8.4	-6.66	-2.08	+1.64	-2.3	65
CF	7.8	-5.69	-1.68	+1.30	-3.5	38
N ₂	5.6	-9.94	-2.35	+1.64	-5.0	50
BF	4.7	-7.91	-1.62	+1.05	-6.0	25
CO	4.0	-11.29	-2.02	+1.22	-7.6	33
CN	3.4	-7.95	-1.33	+0.72	-3.9	51
C ₂	3.1	-6.29	-1.08	+0.56	-0.5	92
B ₂	2.9	-3.07	-0.59	+0.29	-0.8	75
Al ₂	1.5	-1.81	-0.09	+0.02	-0.4	77
CH	1.3	-3.71	-0.61	+0.08	-2.47	33
BH	1.1	-3.62	-0.64	+0.03	-2.7	26
BN	0.7	-5.85	-0.43	-0.06	-2.3	60
H ₂	0.5	-4.79	-1.83	-0.568	-3.6	24
BO	-0.8	-8.27	-0.08	-0.56	-5.8	30
AlH	-1.9	-3.10	+0.10	-0.324	-2.3	27
HF	-2.4	-6.17	+0.42	-1.04	-4.2	32
LiH	-3.9	-2.58	+0.93	-1.57	-1.5	43
SiS	-3.1	-6.48	+0.22	-0.44	-3.9	40
HCl	-3.2	-4.66	+0.28	-0.54	-3.3	29
BeF	-3.4	-6.02	+0.55	-1.01	-5.0	17
Li ₂	-6.9	-1.09	+0.53	-0.72	-0.2	85

NaH	-7.0	-2.16	+0.54	-0.72	-0.9	58
AlO	-8.8	-5.37	+1.00	-1.25	-2.4	55
Cu ₂	-9.0	-2.08	+0.14	-0.18	-0.7	65
AlS	-10.3	-3.86	+0.62	-0.75	-2.5	35
BeO	-14.9	-4.62	+2.68	-3.06	-1.7	64
LiF	-17.0	-6.06	+4.03	-4.54	-3.9	35
NaF	-25.2	-4.98	+3.01	-3.26	-2.9	42
NaCl	-29.9	-4.27	+2.21	-2.36	-3.0	29
H ⁻	-33.1	-0.75	+6.05	-6.42	+0.33	144
Na ₂	-35.2	-0.77	+0.60	-0.63	+0.03	104
CsCl	-39.8	-4.55	+1.23	-1.29	-3.36 ^f	26
KBr	-70.9	-3.96	+2.56	-2.64	-2.97 ^f	25
CsI	-103.0	-3.50	+1.65	-1.68	-2.79 ^f	20
Cs ₂	-131.3	-0.48	+0.28	-0.29	+0.23 ^f	149

^a The spin multiplicity is that of the ground state. ^b Experimental data from NIST Chemistry WebBook. $\Delta E \approx \Delta H^0 - E_{\text{ZPE}}$, where $E_{\text{ZPE}} = \frac{1}{2}h\sum v_i$. ^c From LC-BLYP/aug-cc-pVQZ calculations. Exceptions are H and H₂, where the experimental values of $\bar{\chi}_{\text{H}} = -13.598$ eV and $\bar{\chi}_{\text{H}_2} = -15.426$ eV were used. CsCl, KBr, CsI, Cs₂ and I₂ were calculated using a Douglas-Kroll-Hess 2nd order scalar relativistic Hamiltonian and the ANO-RCC basis set. All noble gas-dimers where calculated using a Douglas-Kroll-Hess 2nd order scalar relativistic Hamiltonian and the QZP-DKH basis set. ^d Correlation energy defined as the difference between the Hartree-Fock and experimental bond dissociation energies. ^e $\Delta E \approx \Delta H^0$ as E_{ZPE} can be presumed small, and no vibrational data is available for Be₂. ^f Calculated using a Douglas-Kroll-Hess 2nd order scalar relativistic Hamiltonian and the basis set specified in footnote c.

Tentative Relationship Between Q and Overlap of Atomic Orbitals

TABLE S3. Molecules with predicted high covalency (Q near 1) hints at a relation with the spatial overlap of atomic orbitals.

Bond	$d_{\text{exp}} [\text{\AA}]$	Q	Bond orbital type
BH	1.232	1.1	$2p-1s, \sigma_u$
^3BN	1.281	0.7	$2p-2p, \sigma_g$
H_2	0.741	0.5	$1s-1s, \sigma_g$
Al_2	2.466	1.5	$3p-3p, \sigma_g$

Comments on the Possibility of Scaled Measures of Covalency (0-100%)

The concept of “covalency” might be thought of as a percentage, or fraction of a whole. Because the Q scale (Eq. S0) is unbound and because it has a *sign* which allows for two ways of diverging from the “perfectly covalent” case at Q = 1, the Q scale inherently conveys more information than any arbitrarily bound percentage value for covalency could.

$$Q = \frac{\overbrace{\Delta\bar{\chi}}^{\text{"covalency"}}}{\Delta E / n} - \frac{\overbrace{\Delta(V_{NN} + \omega) / n}^{\text{multielectron-contribution}}}{\Delta E / n} = \frac{\Delta\bar{\chi} - \Delta(V_{NN} + \omega) / n}{\Delta\bar{\chi} + \Delta(V_{NN} + \omega) / n} = \frac{K - 1}{K + 1} = \frac{2n\Delta\bar{\chi}}{\Delta E} - 1$$

$$K = \frac{\Delta\bar{\chi}}{\Delta(V_{NN} + \omega) / n} \quad (\text{S0})$$

If one is willing to live without this extra information, one can introduce different arbitrary scaling formulations for Q that, for instance, constrain the scale between zero and one hundred percent. We do not advise this, we merely comment on the possibility. Different approaches to the arbitrary scaling of Q can be conceived by basing a measure of covalency on the two units of Q within the range -1.0 < Q < 1.0,

$$Q - \text{Covalence (0-100\%)} = 100 \times \left(1 - \frac{|Q - 1|}{2 + |Q - 1|} \right) \quad (\text{S1})$$

Equation S1 could serve the purpose of connecting the intuitively engrained concept of bond covalency as a fraction or percentage to the measure of bond character that is Q. The quite significant downside is, again, that the sign of Q (which is informative) is lost. A further downside with the scaling described by equation S1 handles the singularity at Q = -1 by forcing a value of 50% at this point. As have been argued in the main text the covalency at Q = -1 should equal 0%, because at this point $\Delta E = \Delta(V_{NN} + \omega)/n$ and $\Delta\bar{\chi} = 0$.

Expressing Covalency (0-100 %) as a function of $\Delta(V_{NN} + \omega)/n$ and $\Delta\bar{\chi}$

Another formulation (not based on Q) that makes away with the singularity is given by equation S2.

$$\text{Covalency (\%)} = \underbrace{\frac{100 \times (|\Delta\bar{\chi}| - \Delta\bar{\chi})}{2} \times \left(\frac{1}{|(\Delta V_{NN} + \Delta\omega) / n| - \Delta\bar{\chi}} \right)}_{\text{active for nuclear-resisted bonds}} + \underbrace{\frac{100 \times (|\Delta\bar{\chi}| + \Delta\bar{\chi})}{2} \times \left(\frac{1}{(\Delta V_{NN} + \Delta\omega) / n} + \frac{1}{\Delta\bar{\chi}} \right)}_{\text{active for multielectron-favored bonds}} \quad (\text{S2})$$

In this formulation, covalence is expressed differently depending whether the bond in question is nuclear-resisted ($\Delta\bar{\chi} < 0$) or multielectron-favored ($\Delta\bar{\chi} > 0$). Nuclear favored bonds are here constrained from 50-100%, and multielectron-favored bond range from 0-50%. Quite chemically reasonable values are obtained, as shown by Table S4. H₂, HF and NaCl, are for instance classified as 76, 59 and 6% covalent, respectively.

TABLE S4. Example “covalency” percentages calculated using equation S2.

Species ^a	Q	Covalency (%)
BH	1.1	95.2
CH	1.3	88.6
BN	0.7	87.4
Al ₂	1.5	83.4
H ₂	0.5	76.3

AlH	-1.9	68.3
B ₂	2.9	67.4
C ₂	3.1	66.0
CN	3.4	64.9
CO	4.0	62.4
BF	4.7	60.6
HF	-2.4	59.3
N ₂	5.6	58.9
CF	7.8	56.4
NO	8.4	56.0
O ₂	9.3	55.4
Cl ₂	10.4	54.8
NF	11.3	54.4
H ₂ ⁺	11.3	54.4
Be ₂	13.2	53.8
ClF	13.0	53.8
OF	14.2	53.5
F ₂	16.0	53.1
I ₂	24.8	52.0
He ₂	~29	51.7
Ar ₂	~37	51.4
Kr ₂	~57	50.9
Xe ₂	~57	50.9
Ne ₂	~79	50.6
SiS	-3.1	49.3
HCl	-3.2	47.6
BeF	-3.4	45.8
LiH	-3.9	41.0
Li ₂	-6.9	25.3
NaH	-7.0	24.9
AlO	-8.8	20.4
Cu ₂	-9.0	20.0
AlS	-10.3	17.8
BeO	-14.9	12.6
BO	-0.8	11.8
LiF	-17.0	11.1
NaF	-25.2	7.6
NaCl	-29.9	6.5
H ⁻	-33.1	5.9
Na ₂	-35.2	5.5
CsCl	-39.8	4.9
KBr	-70.9	2.8

CsI	-103.0	1.9
Cs ₂	-131.3	1.5
