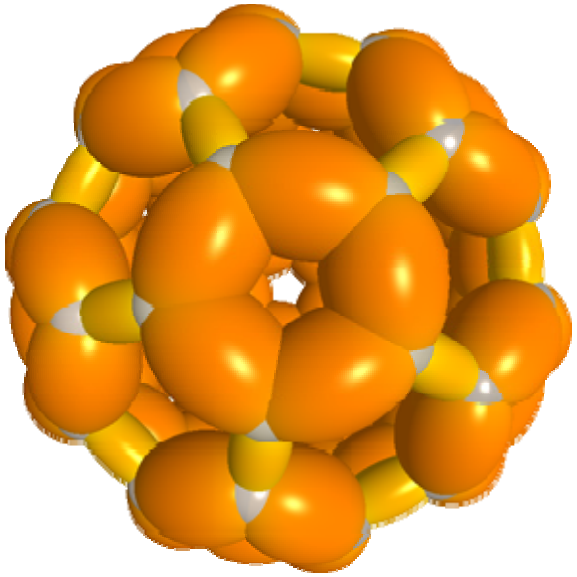
The

Grand Unified Theory

of

Classical Physics

February 2011



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Part 2:

Molecular Physics

The Nature of the Chemical Bond of Hydrogen

The Laplacian in ellipsoidal coordinates is solved with the constraint of nonradiation

$$(\eta-\zeta)R_\xi\frac{\delta}{\delta\xi}(R_\xi\frac{\delta\phi}{\delta\xi})+(\zeta-\xi)R_\eta\frac{\delta}{\delta\eta}(R_\eta\frac{\delta\phi}{\delta\eta})+(\xi-\eta)R_\zeta\frac{\delta}{\delta\zeta}(R_\zeta\frac{\delta\phi}{\delta\zeta})=0$$

The Force Balance Equation for the Hydrogen Molecule

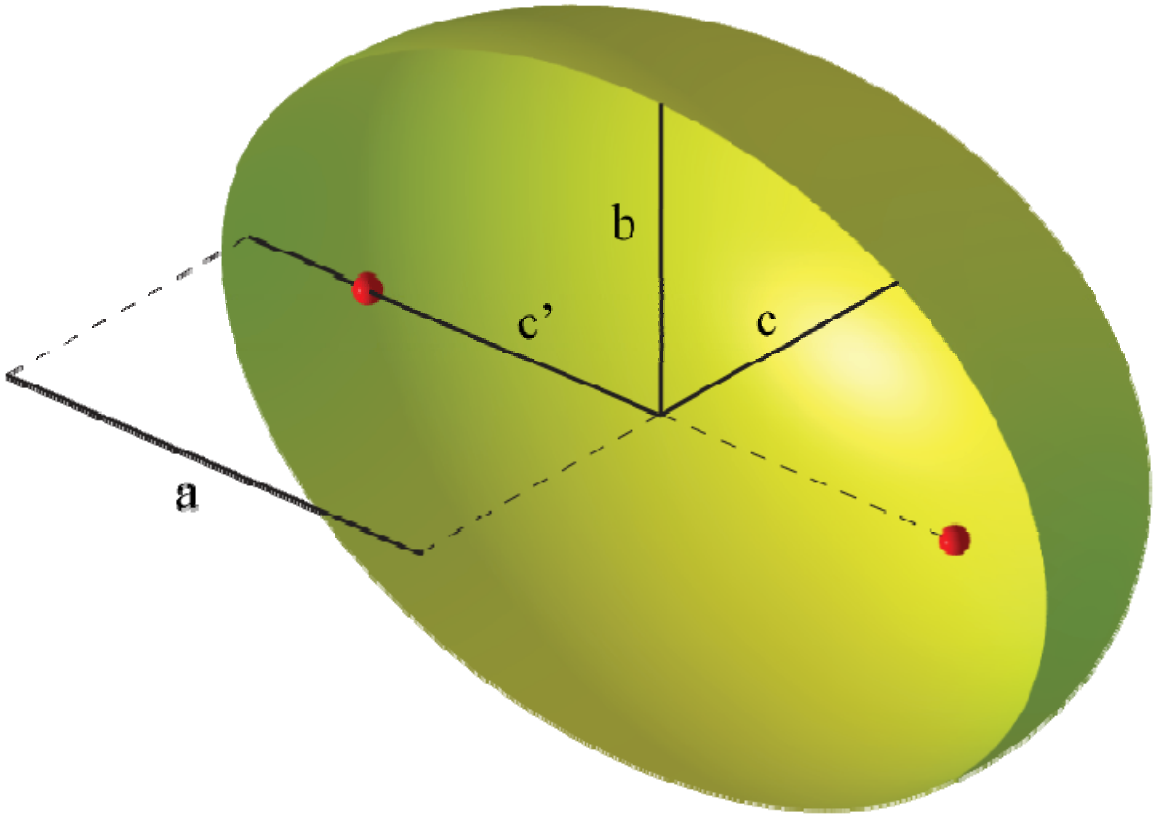
$$\frac{\hbar^2}{m_e a^2 b^2}D=\frac{e^2}{8\pi\varepsilon_o ab^2}D+\frac{\hbar^2}{2m_e a^2 b^2}D$$

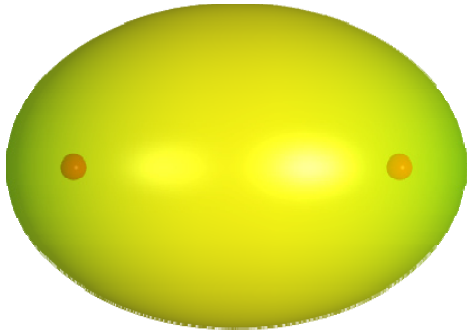
where $D=r(t)$ is the distance from the origin to the ellipsoid

$r(t)$ has the parametric solution $r(t)=\mathbf{i}a\cos\omega t+\mathbf{j}b\sin\omega t$

When the **Semimajor Axis**, a, **is** $a=a_o$

The Nature of the Chemical Bond of Hydrogen cont'd





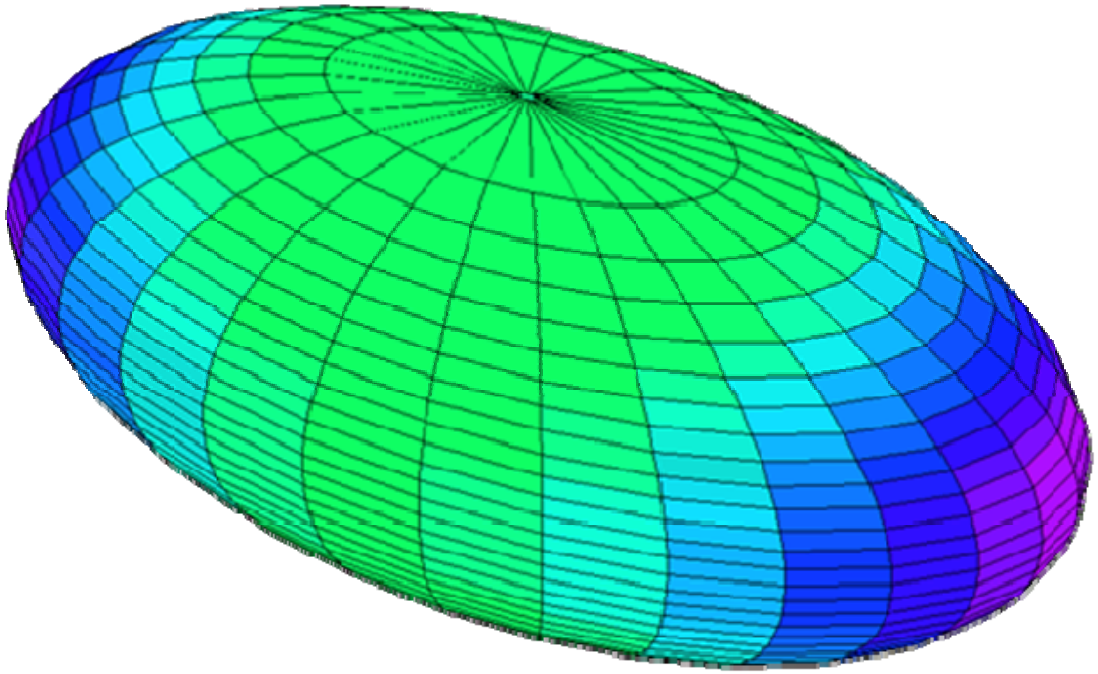
Front view

The Internuclear Distance, $2c'$, which is the distance between the foci is $2c' = \sqrt{2}a_o$.

The experimental internuclear distance is $\sqrt{2}a_o$.

The Semiminor Axis, *b*, is $b = \frac{1}{\sqrt{2}}a_o$ The Eccentricity, *e*, is $e = \frac{1}{\sqrt{2}}$

Charge-Density Function



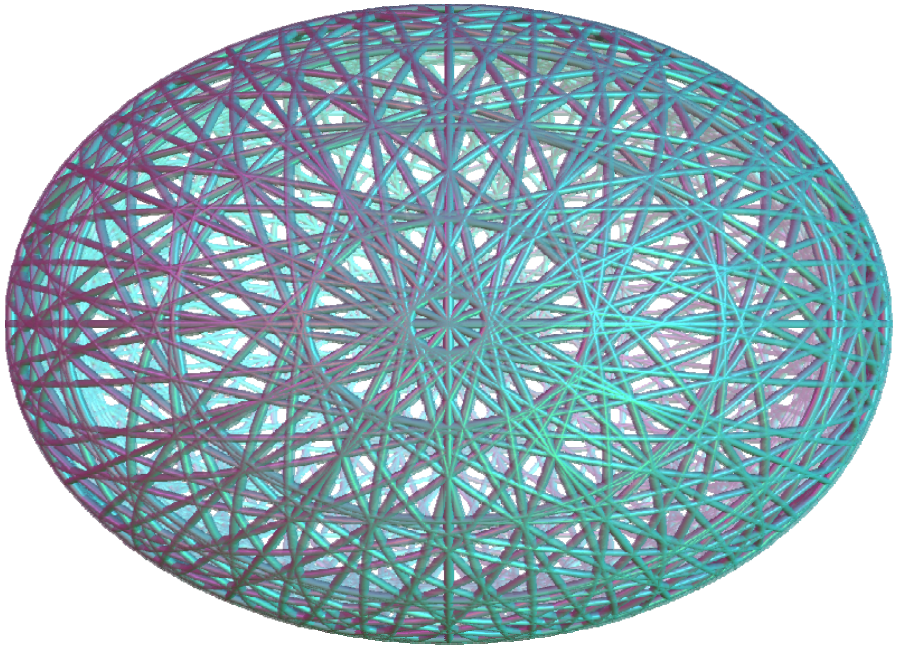




Molecular Orbital Current Corresponding to Electron Spin s=1/2

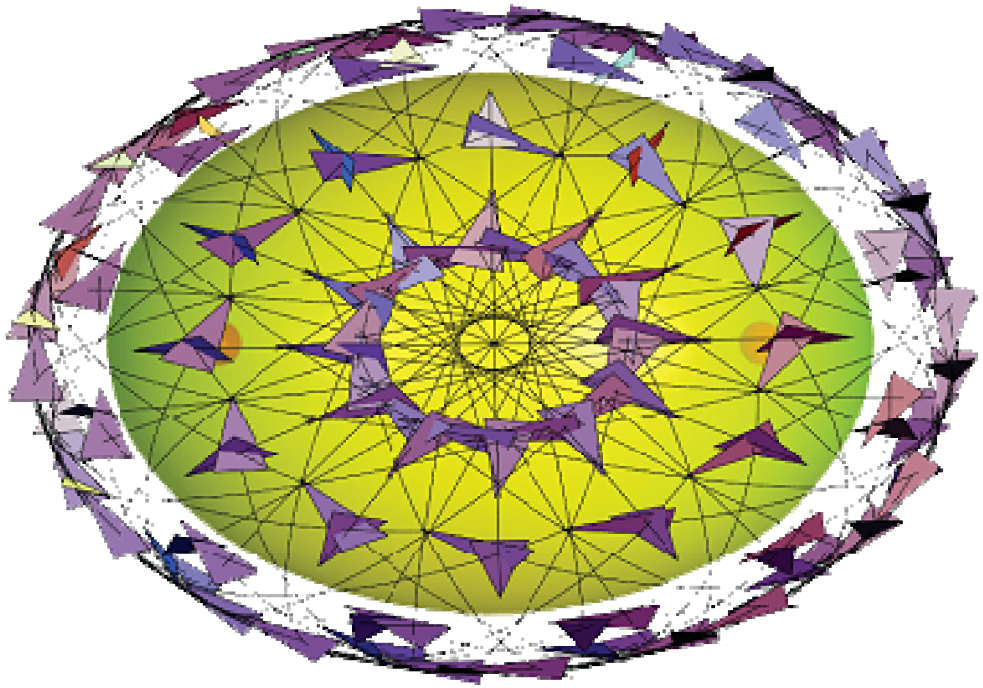
The bound electron MO, a prolate spheroidal two-dimensional supercurrent comprising an extended continuous distribution of charge and current completely surrounding the nuclei at the foci, obtained by stretching $Y_0^0\left(\theta,\phi\right)$ along the semi-major axis. Unlike a spinning top, there is a complex pattern of motion on its surface that generates two orthogonal components of angular momentum that give rise to the phenomenon of electron spin.

Molecular Orbital Current Corresponding to Electron Spin s=1/2



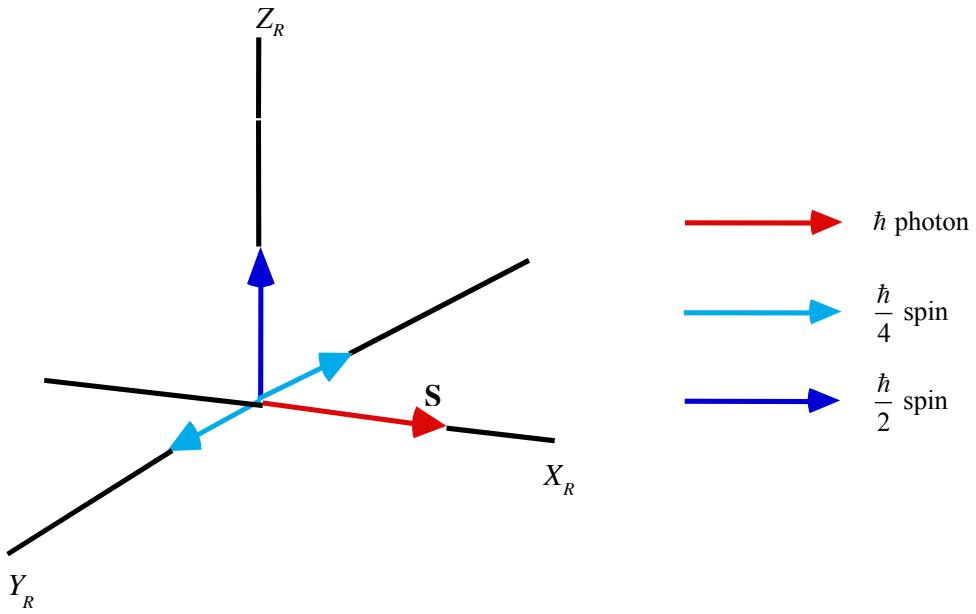
The z-axis view of the MO current paths having $\mathbf{L}_z = \frac{\hbar}{2}$ matching the angular momentum projection on the $\left(-\frac{1}{\sqrt{2}}\mathbf{i_x}, \frac{1}{\sqrt{2}}\mathbf{i_y}, \mathbf{i_z}\right)$-axis of the basis element $Y_0^0(\theta,\phi)$.

Molecular Orbital Current Corresponding to Electron Spin s=1/2



A representation of the z-axis view of the continuous charge-density and supercurrent-density distributions of the MO with 144 vectors overlaid giving the direction of the currents (nuclei not to scale).

Molecular Orbital Current Corresponding to Electron Spin s=1/2



The angular momentum components of the MO and $\mathbf{S}=\hbar$ following Larmor excitation in the rotating coordinate system X_R, Y_R, and Z_R that precesses at the Larmor frequency about $\mathbf{S}$ such that the $\mathbf{S}$ vector is stationary.

The Energies of the Hydrogen Molecule

The Potential Energy of the Two Electrons in the Central Field of the Protons at the Foci

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.8358\,eV$$

The Potential Energy of the Two Protons

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} = 19.2415\,eV$$

The Kinetic Energy of the Electrons

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179\,eV$$

The Energy, V_m, of the Magnetic Force Between the Electrons

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.9589\,eV$$

The Energies of the Hydrogen Molecule cont'd

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the protons. The corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies.

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

The Total Energy of the Hydrogen Molecule

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -13.60\,eV\left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2}\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = -31.689\,eV$$

The calculated and experimental parameters of H_2, D_2, H_2^+ and D_2^+.

Parameter	Calculated	Experimental	Eqs.[a]
H_2 Bond Energy	4.478 eV	4.478 eV	12.251
D_2 Bond Energy	4.556 eV	4.556 eV	12.253
H_2^+ Bond Energy	2.654 eV	2.651 eV	12.220
D_2^+ Bond Energy	2.696 eV	2.691 eV	12.222
H_2 Total Energy	31.677 eV	31.675 eV	12.247
D_2 Total Energy	31.760 eV	31.760 eV	12.248
H_2 Ionization Energy	15.425 eV	15.426 eV	12.249
D_2 Ionization Energy	15.463 eV	15.466 eV	12.250
H_2^+ Ionization Energy	16.253 eV	16.250 eV	12.218
D_2^+ Ionization Energy	16.299 eV	16.294 eV	12.219
H_2^+ Magnetic Moment	$9.274\,X\,10^{-24}\,JT^{-1}$ μ_B	$9.274\,X\,10^{-24}\,JT^{-1}$ μ_B	14.1-14.7
Absolute H_2 Gas-Phase NMR Shift	-28.0 ppm	-28.0 ppm	12.362
H_2 Internuclear Distance[b]	0.748 Å $\sqrt{2}a_o$	0.741 Å	12.238
D_2 Internuclear Distance[b]	0.748 Å $\sqrt{2}a_o$	0.741 Å	12.238
H_2^+ Internuclear Distance[c]	1.058 Å $2a_o$	1.06 Å	12.207
D_2^+ Internuclear Distance[b]	1.058 Å $2a_o$	1.0559 Å	12.207
H_2 Vibrational Energy	0.517 eV	0.516 eV	12.259
D_2 Vibrational Energy	0.371 eV	0.371 eV	12.264
H_2 $\omega_e x_e$	120.4 cm^{-1}	121.33 cm^{-1}	12.261
D_2 $\omega_e x_e$	60.93 cm^{-1}	61.82 cm^{-1}	12.265
H_2^+ Vibrational Energy	0.270 eV	0.271 eV	12.228
D_2^+ Vibrational Energy	0.193 eV	0.196 eV	12.232
H_2 J=1 to J=0 Rotational Energy[b]	0.0148 eV	0.01509 eV	14.45
D_2 J=1 to J=0 Rotational Energy[b]	0.00741 eV	0.00755 eV	14.37-14.45
H_2^+ J=1 to J=0 Rotational Energy[c]	0.00740 eV	0.00739 eV	14.49
D_2^+ J=1 to J=0 Rotational Energy[b]	0.00370 eV	0.003723 eV	14.37-14.43, 14.49

[a] R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, September 2001 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by Amazon.com; January (2003) Edition posted at www.blacklightpower.com.

[b] The internuclear distances are not corrected for the reduction due to $\overline{E}_{osc}$.

[c] The internuclear distances are not corrected for the increase due to $\overline{E}_{osc}$.

Excited States of the Hydrogen Molecule

Excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO of the outer excited-state electron.

The excited-state photon's ellipsoidal electric field at the outer electron superimposes that of the net field of the nuclei at the foci of the inner MO and inner MO charge such that the net electric field has a magnitude proportional to Z/n in the direction of $\mathbf{i}_\xi$ at the outer electron where $n = 2,3,4\ldots$ for excited states.

Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces with an increased distance ξ.

Then, the force balance of the outer excited-state electron is given by balance between the centrifugal force, the central Coulombic force corresponding to the effective central field due to the superposition of photon field at the outer electron and the net field of the protons at the foci of the inner MO, and the magnetic forces for the particular spin and orbital state.

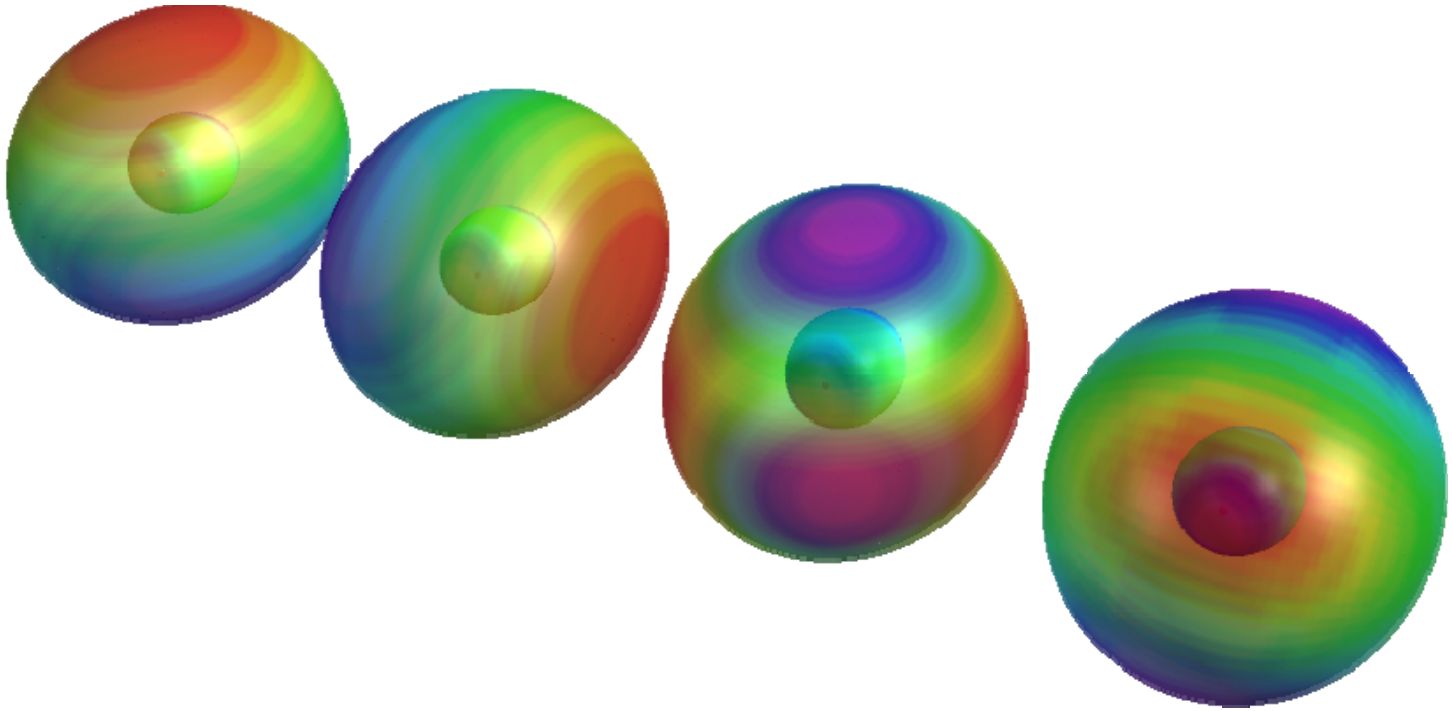
The geometrical parameters for H_2 excited states are determined from the semimajor axis given by the force balance and the relationships among the ellipsoidal parameters.

•Overhead-view of exemplary color scale, translucent views of the charge-densities of the inner and outer electrons of molecular-hydrogen excited states.

•The ellipsoidal-spherical harmonic modulation functions propagate about the major axis as spatially and temporally harmonic charge-density waves.

• The corresponding orbital function of the outer-electron modulates the time-constant (spin) function, (shown for t = 0; three-dimensional view).

• The inner electron is essentially that of H_2^+ (nuclei red, not to scale).



Excited States of the Hydrogen Molecule

Singlet Excited States $\ell = 0$

The force balance between the electric, magnetic, and centrifugal forces of the outer electron given is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_o a b^2} D + \frac{1}{n} \frac{2m}{3} \frac{1}{2} \frac{\hbar^2}{2 m_e a^2 b^2} D$$

m is a positive or negative integer .

The semimajor axis, a, is

$$a = a_0 \left(2n - \frac{m}{3} \right)$$

The internuclear distance, $2c'$, is

$$2c' = 2\sqrt{\frac{a a_0}{2p}} = 2a_0 \sqrt{\frac{n\left(2n - \frac{m}{3} \right)}{2}}$$

The semiminor axis is

$$b = \sqrt{a^2 - c'^2} = a_0 \left(2n - \frac{m}{3} \right) \sqrt{1 - \frac{n}{2\left(2n - \frac{m}{3} \right)}}$$

The eccentricity, e, is

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{m}{3} \right)}}$$

Excited States of the Hydrogen Molecule

Singlet Excited States $\ell \neq 0$

The force balance between the electric, magnetic, and centrifugal forces of the outer electron is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_o ab^2} D + \frac{1}{n} \frac{m}{3} \frac{\hbar^2}{2m_e a^2 b^2} D - \frac{1}{n} \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \frac{1}{2} \frac{\hbar^2}{m_e a^2 b^2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) D$$

The semimajor axis, a, is

$$a = a_0 \left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) \right)$$

The internuclear distance, $2c'$, is

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0 \sqrt{\frac{n\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) \right)}{2}}$$

The semiminor axis is

$$b = \sqrt{a^2 - c'^2} = a_0 \left(\frac{\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) \right)}{\sqrt{1 - \frac{n}{2\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) \right)}}} \right)$$

The eccentricity, e, is

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell} \right)^{1/2} \frac{1}{\ell+2} \left(1 - \sqrt{\frac{\ell}{\ell+1}} \right) \right)}}$$

Excited States of the Hydrogen Molecule

Triplet Excited States $\ell = 0$

The force balance between the electric, magnetic, and centrifugal forces of the outer electron is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_o a b^2} D + \frac{1}{n} \frac{4m}{3} \frac{1}{2} \frac{\hbar^2}{2 m_e a^2 b^2} D$$

The semimajor axis, a, is

$$a = a_0 \left(2n - \frac{2m}{3} \right)$$

The internuclear distance, $2c'$, is

$$2c' = 2\sqrt{\frac{a a_0}{2p}} = 2a_0 \sqrt{\frac{n\left(2n - \frac{2m}{3} \right)}{2}}$$

The semiminor axis is

$$b = \sqrt{a^2 - c'^2} = a_0 \left(2n - \frac{2m}{3} \right) \sqrt{1 - \frac{n}{2\left(2n - \frac{2m}{3} \right)}}$$

The eccentricity, e, is

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{2m}{3} \right)}}$$

Excited States of the Hydrogen Molecule

Triplet Excited States $\ell \neq 0$

The force balance between the electric, magnetic, and centrifugal forces of the outer electron is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_o a b^2} D + \frac{1}{n} \frac{2m}{3} \frac{\hbar^2}{2m_e a^2 b^2} D + \frac{1}{n} \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \frac{1}{2} \frac{\hbar^2}{m_e a^2 b^2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right) D$$

The semimajor axis, a, is

$$a = a_0 \left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right)\right)$$

The internuclear distance, $2c'$, is

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0 \sqrt{\frac{n\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right)\right)}{2}}$$

The semiminor axis is

$$b = \sqrt{a^2 - c'^2} = a_0 \left(\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right)\right) \sqrt{1 - \frac{n}{2\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right)\right)}} \right)$$

The eccentricity, e, is

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!} \left(\frac{\ell+1}{\ell}\right)^{1/2} \frac{1}{\ell+2} \left(2 - \sqrt{\frac{\ell}{\ell+1}}\right)\right)}}$$

Energies of the Excited States of the Hydrogen Molecule

The component energies of the outer electron of the hydrogen molecule of the excited state corresponding to quantum number n are those of H_2 except that the energies are each multiplied by a factor of ½ since the outer MO comprises only one electron, and those corresponding to charge are multiplied by effective-charge factor of $1/n$:

$$V_e = \frac{1}{n}\frac{1}{2}\frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$

$$V_p = 0$$

$$T = \frac{1}{2}\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$

$$V_m = \frac{1}{n}\frac{1}{2}\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$

$$\overline{E}_{osc}\left(H_2\right) = \overline{E}_D + \overline{E}_{Kvib} = -\left(V_e + T + V_m + V\right)\sqrt{\frac{2\hbar\sqrt{\frac{1}{n^4}\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}} + \overline{E}_{Kvib}$$

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\left(\frac{-e^2}{8\pi\varepsilon_o} - \frac{n\hbar^2}{4m_e a} + \frac{\hbar^2}{8m_e a}\right)\frac{1}{n\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{n^4 8\pi\varepsilon_o a_0^3}}}{m_e c^2}}\right] - \overline{E}_{Kvib}\right\}$$

The energy T_e from the n=1 state (also referred to as the state X) to the energy of the n^{th} excited state is given by the sum of E_T and IP_1 of H_2 :

$$T_e\left(H_2\right) = E_T + 15.4248\ eV$$

Excited States of the Hydrogen Molecule

The geometrical and energy parameters of the singlet excited states of molecular hydrogen compared to the experimental energies.

n	m	l	$a\ (a_0)$	$b,c\ (a_0)$	$2c'\ (a_0)$	e	$V_e\ (eV)$	$V_p\ (eV)$	$T\ (eV)$	$V_m\ (eV)$	$E_T(H_2MO)\ (eV)$	$\bar{E}_{osc}\ (eV)$	$Cal.\ T_e\ (eV)$	$Exp.\ T_e\ (eV)$	State	Relative Error
2	4	1	2.73570	2.17907	3.30799	0.60460	-5.76118	0	2.10592	-0.52648	-4.18174	0.12425	11.3673	11.36819	B	0.00008
2	1	1	3.73570	3.19684	3.86559	0.51739	-4.03193	0	1.07930	-0.26982	-3.22245	0.12841	12.3308	12.40385	C	0.00589
2	0	0	4.00000	3.46410	4.00000	0.50000	-3.73688	0	0.93422	-0.23355	-3.03621	0.12922	12.5178	12.40631	E	-0.00899
2	-2	0	4.66667	4.13656	4.32049	0.46291	-3.15548	0	0.67618	-0.16904	-2.64835	0.13091	12.9074	12.82999	F	-0.00603
3	4	0	4.66667	3.84419	5.29150	0.56695	-2.20446	0	0.70858	-0.11810	-1.61398	0.13773	13.9486	13.96780	K	0.00138
3	4	1	4.73570	3.91450	5.33050	0.56280	-2.16761	0	0.68657	-0.11443	-1.59546	0.13778	13.9671	13.98466	G	0.00125
3	3	0	5.00000	4.18330	5.47723	0.54772	-2.03734	0	0.61120	-0.10187	-1.52801	0.13798	14.0348	14.01839	I	-0.00117
3	3	2	5.00562	4.18901	5.48030	0.54742	-2.03474	0	0.60974	-0.10162	-1.52663	0.13798	14.0362	14.02818	Q	-0.00057
3	3	1	5.06904	4.25342	5.51491	0.54398	-2.00588	0	0.59357	-0.09893	-1.51124	0.13803	14.0516	14.06042	J	0.00063
3	2	0	5.33333	4.52155	5.65685	0.53033	-1.89402	0	0.53269	-0.08878	-1.45011	0.13820	14.1129	14.12043	D	0.00053
3	2	1	5.40237	4.59152	5.69335	0.52693	-1.86685	0	0.51834	-0.08639	-1.43490	0.13825	14.1282	14.12055	H	-0.00054
3	1	0	5.66667	4.85913	5.83095	0.51450	-1.76971	0	0.46845	-0.07808	-1.37933	0.13841	14.1839	14.19631	L	0.00087
3	1	1	5.73570	4.92897	5.86636	0.51139	-1.74599	0	0.45661	-0.07610	-1.36548	0.13845	14.1978	14.21540	M	0.00124
3	-3	1	7.06904	6.27437	6.51262	0.46064	-1.38755	0	0.29443	-0.04907	-1.14219	0.13909	14.4217	14.41551	N	-0.00043
4	4	1	6.73570	5.64786	7.34068	0.54491	-1.13268	0	0.33632	-0.04204	-0.83840	0.14058	14.7270	14.71581	R	-0.00076
4	1	2	7.67229	6.59692	7.83443	0.51057	-0.97861	0	0.25510	-0.03189	-0.75539	0.14076	14.8102	14.81549	T	0.00036
4	1	1	7.73570	6.66106	7.86674	0.50847	-0.96969	0	0.25070	-0.03134	-0.75032	0.14077	14.8153	14.81772	P	0.00017
4	-1	0	8.33333	7.26483	8.16497	0.48990	-0.89305	0	0.21433	-0.02679	-0.70551	0.14087	14.8602	14.85591	S	-0.00029
4	-1	1	8.40237	7.33451	8.19872	0.48788	-0.88497	0	0.21065	-0.02633	-0.70066	0.14088	14.8650	14.85975	O	-0.00036
															Avg. Rel. Error	-0.00035

Excited States of the Hydrogen Molecule

The geometrical and energy parameters of the triplet excited states of molecular hydrogen compared to the experimental energies.

n	m	l	$a\ (a_0)$	$b,c\ (a_0)$	$2c'\ (a_0)$	e	$V_e\ (eV)$	$V_p\ (eV)$	$T\ (eV)$	$V_m\ (eV)$	$E_T(H_2MO)\ (eV)$	$\bar{E}_{osc}\ (eV)$	$Cal.\ T_e\ (eV)$	$Exp.\ T_e\ (eV)$	State	Relative Error
2	1	1	3.02860	2.47867	3.48057	0.57462	-5.11612	0	1.68927	-0.42232	-3.84916	0.12570	11.7013	11.87084	c	0.01428
2	1	0	3.33333	2.78887	3.65148	0.54772	-4.58402	0	1.37520	-0.34380	-3.55261	0.12698	11.9992	11.89489	a	-0.00877
3	4	1	3.02860	2.15163	4.26281	0.70376	-3.72248	0	1.84367	-0.30728	-2.18609	0.13607	13.3748	13.36275	e	-0.00090
3	2	2	4.63043	3.80726	5.27092	0.56916	-2.22432	0	0.72056	-0.12009	-1.62386	0.13770	13.9387	13.97338	d	0.00249
3	2	0	4.66667	3.84419	5.29150	0.56695	-2.20446	0	0.70858	-0.11810	-1.61398	0.13773	13.9486	13.98181	h	0.00238
3	1	1	5.02860	4.21235	5.49287	0.54616	-2.02419	0	0.60380	-0.10063	-1.52102	0.13800	14.0418	13.98268	g	-0.00423
3	1	2	5.29710	4.48482	5.63760	0.53214	-1.90861	0	0.54047	-0.09008	-1.45822	0.13818	14.1048	14.01132	i	-0.00667
3	1	0	5.33333	4.52155	5.65685	0.53033	-1.89402	0	0.53269	-0.08878	-1.45011	0.13820	14.1129	14.03488	j	-0.00556
4	4	1	5.02860	3.90251	6.34261	0.63065	-1.59277	0	0.63349	-0.07919	-1.03847	0.14014	14.5265	14.47007	f	-0.00390
4	3	1	5.69526	4.58754	6.74997	0.59260	-1.37400	0	0.48251	-0.06031	-0.95181	0.14033	14.6133	14.66658	v	0.00363
4	3	2	5.96376	4.86199	6.90725	0.57910	-1.30225	0	0.43672	-0.05459	-0.92012	0.14040	14.6451	14.67625	k	0.00212
4	2	1	6.36193	5.26785	7.13410	0.56069	-1.20882	0	0.38002	-0.04750	-0.87630	0.14050	14.6890	14.68915	p	0.00001
4	2	0	6.66667	5.57773	7.30297	0.54772	-1.14600	0	0.34380	-0.04298	-0.84518	0.14056	14.7202	14.69250	s	-0.00189
4	1	1	7.02860	5.94508	7.49858	0.53343	-1.07948	0	0.30717	-0.03840	-0.81070	0.14064	14.7547	14.70155	r	-0.00362
4	1	0	7.33333	6.25389	7.65942	0.52223	-1.02923	0	0.28070	-0.03509	-0.78362	0.14070	14.7819	14.79379	m	0.00080
5	3	1	7.69526	6.32289	8.77226	0.56998	-0.80341	0	0.26101	-0.02610	-0.56850	0.14141	14.9977	14.99651	n	-0.00008
5	3	2	7.96376	6.59637	8.92399	0.56029	-0.77238	0	0.24247	-0.02425	-0.55416	0.14143	15.0121	15.01449	q	0.00016
5	2	1	8.36193	7.00122	9.14436	0.54679	-0.73059	0	0.21843	-0.02184	-0.53401	0.14147	15.0323	15.03879	t	0.00043
6	-4	0	14.66667	13.08094	13.26650	0.45227	-0.33334	0	0.06818	-0.00568	-0.27084	0.14201	15.2960	15.31031	u	0.00094
															Avg. Rel. Error	-0.00044

Exact Solutions of Diatomic and Polyatomic Molecules

- Molecules are solved exactly by using the exact atomic-orbital solutions and the prolate spheroidal molecular orbitals as basis functions.

- The prolate spheroidal MO bridges the AOs and is matched to the energy of the AOs of each bond.

- Alternatively, AO electrons form an independent MO and the remaining electrons of the participating shell decrease in radius and energy.

The semimajor axis is solved from the equation of the form:

$$-\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(AO/HO\right)=E(basis\ energies)$$

The other geometrical parameters are solved from ellipsoidal relationships.

The total bond energy of the group E_D (*Group*) is given by

$$E_D\left(Group\right)=-\left(\begin{array}{l}\left(E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}}\right]\\ +n_1\bar{E}_{Kvib}+c_3\frac{8\pi\mu_o\mu_B^2}{r_n^3}-\left(c_4E_{initial}\left(c_4AO/HO\right)+c_5E_{initial}\left(c_5\ AO/HO\right)\right)\end{array}\right)$$

Exact Solutions of Organic Molecules

- For the first time in history, the functional groups, the key building blocks of organic chemistry, were solved from two basic equations.
- The solutions of the basic **300+ functional groups** of organic chemistry were obtained by using generalized forms of a geometrical and an energy equation for the nature of the H-H bond.
- The true physical structure and parameters of an infinite number of organic molecules up to infinite length and complexity can be obtained essentially instantly.
- There is no algorithm. In contrast, NIST presents 788 molecules for which there are over 100,000 attempted solutions,150 per molecule on average, representing the combined worldwide effort of over half a century. (source: http://srdata.nist.gov/cccbdb/default.htm)
- Millsian modeling software instantaneously provides the physical structure and parameters of organic molecules at higher precision and accuracy than any other commercial product.
- Modeling recently extended to include organometalics, semiconductors, all allotropes of carbon, and metals.

Partial List of Organic Functional Groups Solved by Classical Physics

Continuous-chain alkanes
Branched alkanes
Alkenes
Branched alkenes
Alkynes
Alkyl fluorides
Alkyl chlorides
Alkyl bromides
Alkyl iodides
Alkenyl halides
Aryl halides
Alcohols
Ethers
Primary amines
Secondary amines
Tertiary amines
Aldehydes
Ketones
Carboxylic acids
Carboxylic acid esters
Amides
N-alkyl amides

N,N-dialkyl amides
Urea
Carboxylic acid halides
Carboxylic acid anhydrides
Nitriles
Thiols
Sulfides
Disulfides
Sulfoxides
Sulfones
Sulfites
Sulfates
Nitroalkanes
Alkyl nitrates
Alkyl nitrites
Conjugated alkenes
Conjugated polyenes
Aromatics
Naphthalene
Toluene
Chlorobenzene

Phenol
Aniline
Aryl nitro compounds
Benzoic acid compounds
Anisole
Pyrrole
Furan
Thiophene
Imidizole
Pyridine
Pyrimidine
Pyrazine
Quinoline
Isoquinoline
Indole
Adenine
Fullerene (C_{60})
Graphite
Phosphines
Phosphine oxides
Phosphites
Phosphates

Partial List of Additional Molecules and Compositions of Matter Solved by Classical Physics.

Solid Molecular Bond of the Three Allotropes of Carbon

- Diamond
- Graphite
- Fullerene (C_{60})

Dipole-Dipole Bonding

- Hydrogen Bonding
- Van der Waals Bonding

Solid Ionic Bond of Alkali-Hydrides

- Alkali Hydride Crystal Structures
  - Lithium Hydride
  - Sodium Hydride
  - Potassium Hydride
  - Rubidium & Cesium Hydride
  - Potassium Hydrino Hydride

Solid Metallic Bond of Alkali Metals

- Alkali Metal Crystal Structures
  - Lithium Metal
  - Sodium Metal
  - Potassium Metal
  - Rubidium & Cesium Metals

Alkyl Aluminum Hydrides

Silicon Groups & Molecules

- Silanes
- Alkyl Silanes and Disilanes

Solid Semiconductor Bond of Silicon

- Insulator-Type Semiconductor Bond
- Conductor-Type Semiconductor Bond

Boron Molecules

- Boranes
  - Bridging Bonds of Boranes
- Alkoxy Boranes
- Alkyl Boranes
- Alkyl Borinic Acids
- Tertiary Aminoboranes
- Quaternary Aminoboranes
- Borane Amines
- Halido Boranes

Organometallic Molecular Functional Groups and Molecules

- Alkyl Aluminum Hydrides
  - Bridging Bonds of Organoaluminum Hydrides
- Organogermanium & Digermanium
- Organolead

Organometallic Molecular Functional Groups and Molecules

- Organoarsenic
- Organoantimony
- Organobismuth

Organic Ions

- 1˚Amino
- 2˚Amino
- Carboxylate
- Phosphate
- Nitrate
- Sulfate
- Silicate

Proteins

- Amino Acids
- Peptide Bonds

DNA

- Bases
- 2-deoxyribose
- Ribose
- Phosphate Backbone

Water

Condensed Noble Gases



- Subsidiary founded to develop computational molecule design and simulation software for the life sciences, materials sciences, nanotechnology, and chemical industries
- In a new molecular modeling paper, the energies of exact classical solutions of molecules generated by Millsian 1.0 and those from a modern quantum mechanics-based program were compared to experimental values. The Millsian results were consistently within an average relative deviation of about 0.1% of the experimental values. In contrast, the 3-21G and 6-31G* results deviated over a wide range of relative error, typically being >30-150% with a large percentage of catastrophic failures

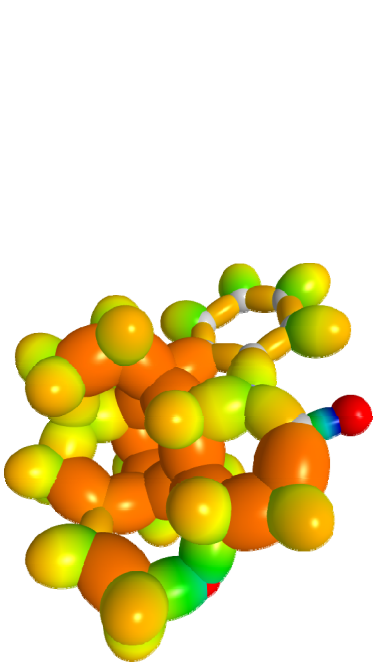
Total Bond Energies of Exact Classical Solutions of Molecules Generated by Millsian 1.0 Compared to Those Computed Using Modern 3-21G and 6-31G* Basis Sets - R.L. Mills, B. Holverstott, W. Good, N. Hogle, A. Makwana

Millsian 2.0

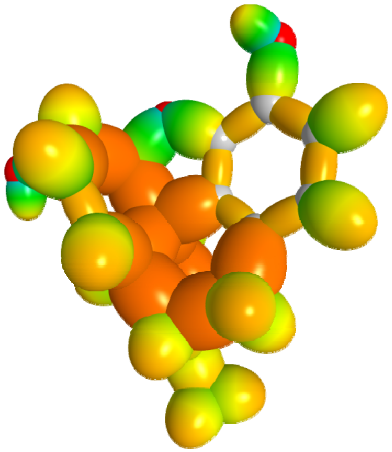
- **Evaluate** molecules for binding sites, reactive sites, and pockets, using our exact charge distribution profiles and optimized molecular structures.
- **Calculate** total bond energy or heat of formation for almost any organic molecule
- **Calculate** optimized molecular structures for molecules, including those not in existing databases. Reduce your reliance on molecular structure databases.
- **Edit** protein structures by auto-detecting missing hydrogens, and use our bond order correction tool for complex molecules like PDB heterogens.
- **Calculate** dipole moments and rotation barrier heights for molecular conformation changes.
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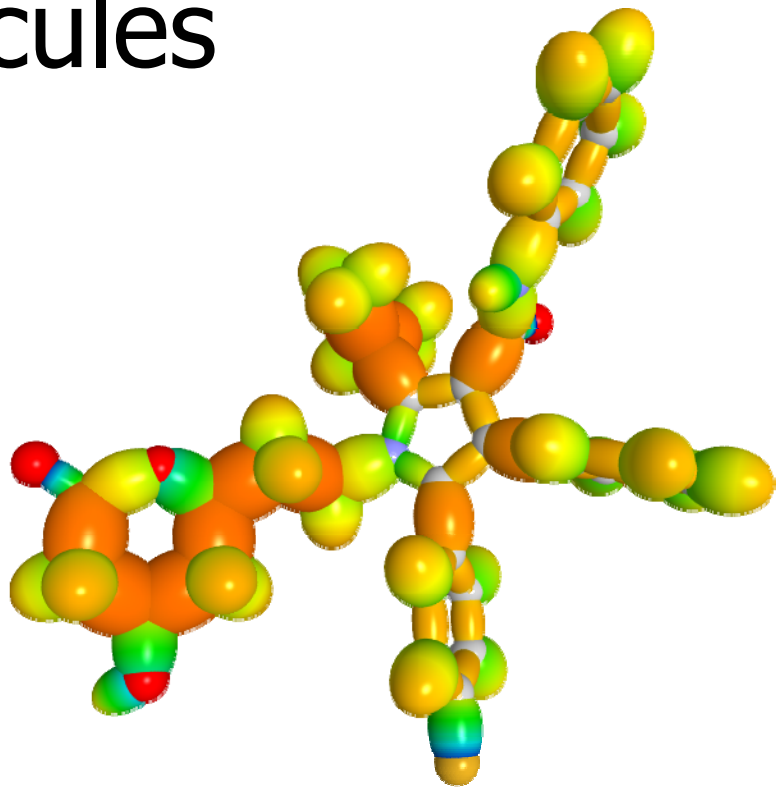
Millsian 2.0:
Drug Molecules



Strychnine

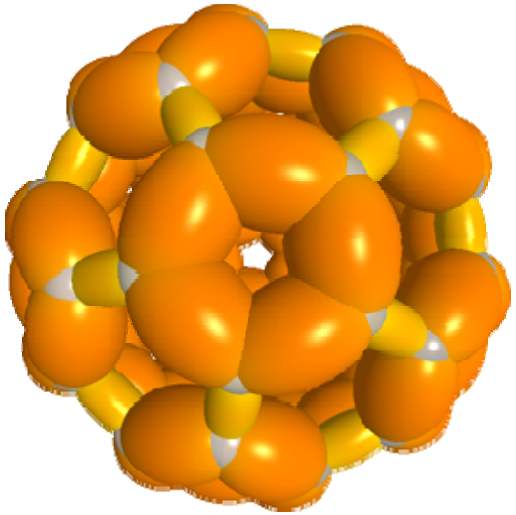


Morphine

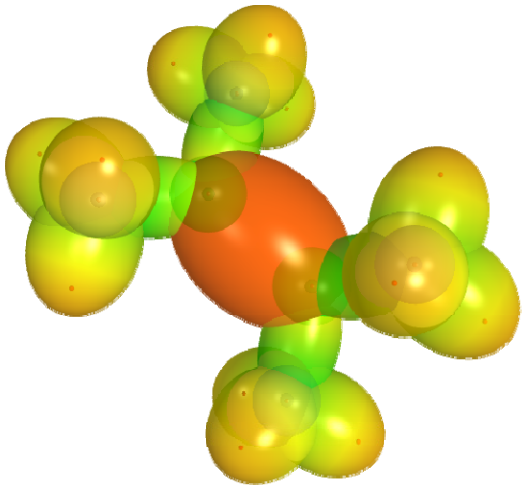


Lipitor

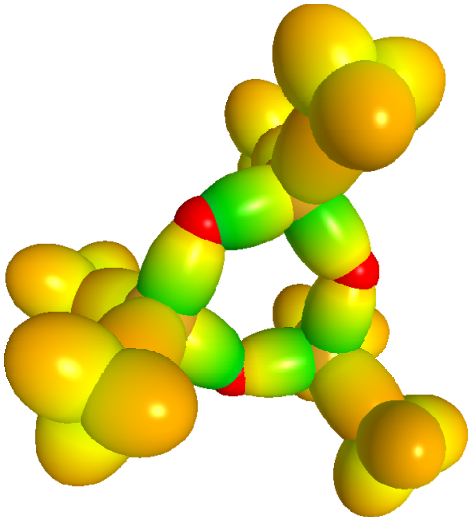
Millsian 2.0:
Other Molecule Classes



Allotropes of Carbon
C_{60} Fullerene

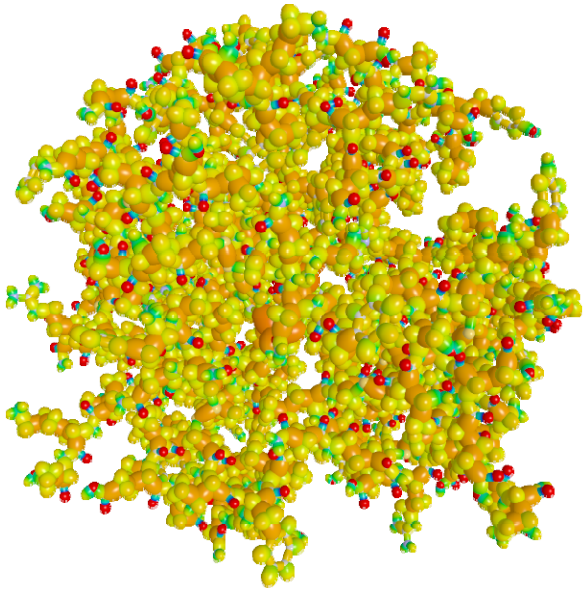


Boron Molecules
Tetramethyldiboron

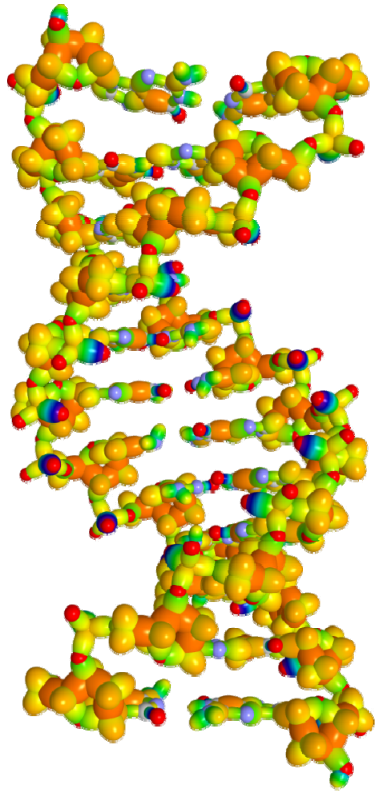


Silicon Molecules
$((CH_3)_2SiO)_3$

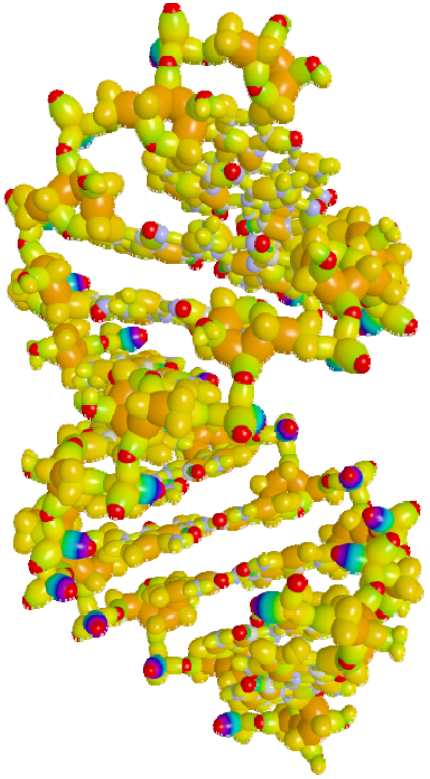
Millsian 2.0:
Large Biomolecules



Insulin



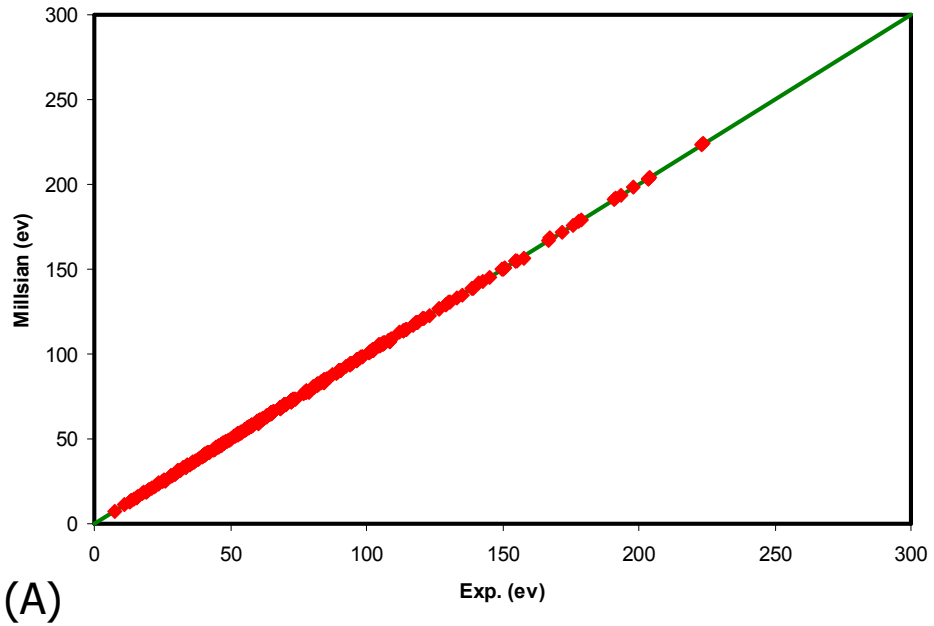
DNA



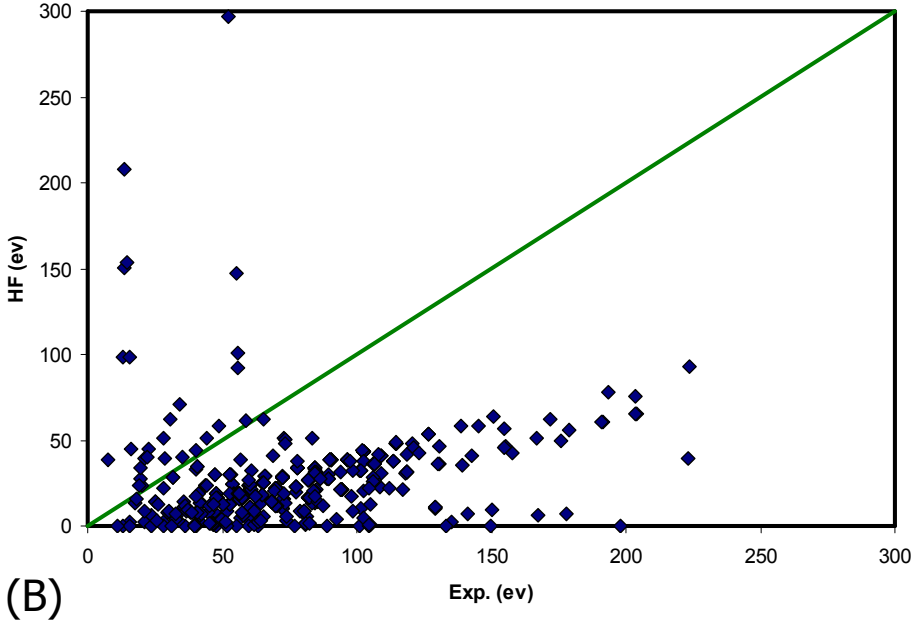
RNA

Comparison of Classical to Quantum Mechanical Performance

The total bond energies of exact classical solutions of 415 molecules generated by Millsian 1.0 and those from a modern quantum mechanics-based program, Spartan's pre-computed database using 6-31G* basis set at the Hartree-Fock level of theory, were compared to experimental values. (A) The Millsian results were consistently within an average relative deviation of about 0.1% of the experimentally values. (B) In contrast, the 6-31G* results deviated over a wide range of relative error, typically being >30-150% with a large percentage of catastrophic failures, depending on functional group type and basis set.



(A)

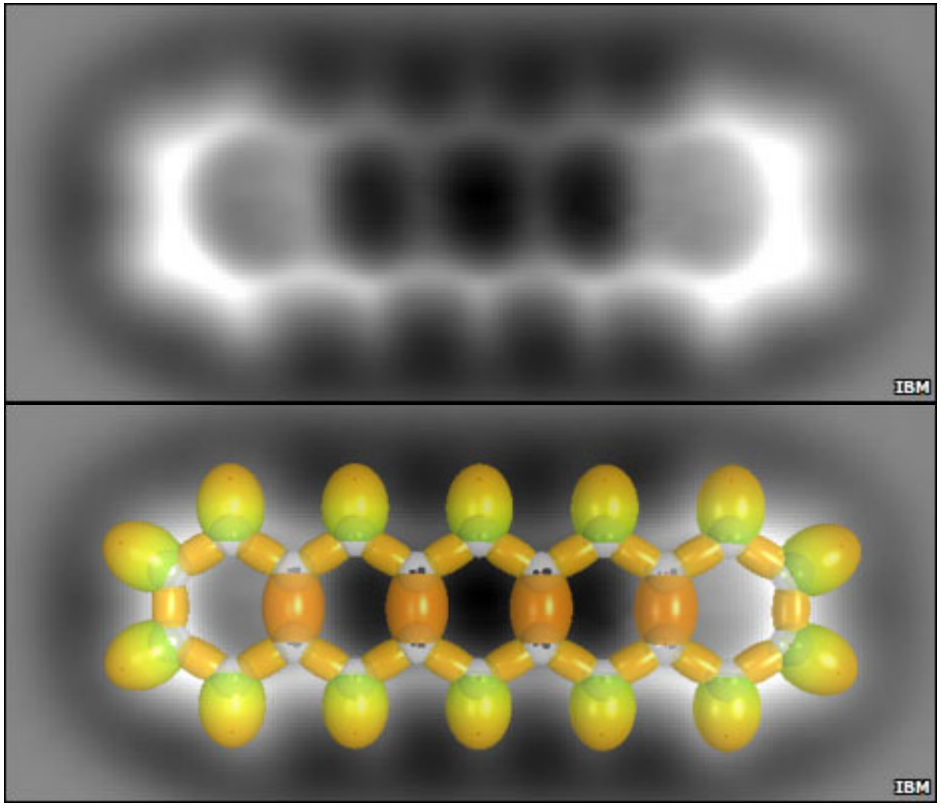


(B)

R. L. Mills, B. Holverstott, W. Good, A. Makwana, J. Paulus, "Total Bond Energies of Exact Classical Solutions of Molecules Generated by Millsian 1.0 Compared to Those Computed Using Modern 3-21G and 6-31G* Basis Sets," Phys. Essays 23, 153 (2010); doi: 10.4006/1.3310832

Physical Image Compared to Physical Solution

The polycyclic aromatic hydrocarbon pentacene was imaged by atomic force microscopy using a single CO molecule as the probe. The resulting breakthrough in resolution revealed that in contrast to the fuzzy images touted by quantum theoreticians as proof of the cloud model of the electron, the images showed localized bonding MOs and AOs in agreement with the classical



Atomic force microscopy image of pentacene by Gross et al. Bottom, the superimposed analytical classical solution that matches the physical structure. [L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, "The chemical structure of a molecule resolved by atomic force microscopy", Science, Vol. 325, (2009), pp. 1110-1114.]

Summary results of n-alkanes.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_8	Propane	41.46896	41.434	-0.00085
C_4H_{10}	Butane	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	90.09976	90.09	-0.00013
C_8H_{18}	Octane	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	223.83446	223.85	0.00008

Summary results of branched alkanes.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_{10}	Isobutane	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	90.17232	90.108	-0.00072
C_7H_{16}	2,2-Dimethylpentane	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C_7H_{16}	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	102.33002	102.274	-0.00055
C_8H_{18}	2,2-Dimethylhexane	102.33646	102.417	0.00079

Summary results of branched alkanes continued.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_8H_{18}	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C_8H_{18}	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	102.33646	102.369	0.00032
C_8H_{18}	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C_8H_{18}	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C_8H_{18}	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C_8H_{18}	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C_8H_{18}	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C_9H_{20}	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C_9H_{20}	3,3-Diethylpentane	114.49416	114.455	-0.00034
C_9H_{20}	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C_9H_{20}	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024
C_9H_{20}	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	126.64542	126.663	0.00014

Summary results of alkenes.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	35.56033	35.63207	0.00201
C_4H_8	1-Butene	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	59.87573	59.95094	0.00125
C_5H_{10}	trans-2-Pentene	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	60.06084	60.09707	0.00060
C_5H_{10}	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	59.97662	60.01727	0.00068
C_6H_{12}	1-Hexene	72.03343	72.12954	0.00133
C_6H_{12}	trans-2-Hexene	72.24656	72.23733	-0.00013
C_6H_{12}	trans-3-Hexene	72.24656	72.24251	-0.00006
C_6H_{12}	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043

Summary results of alkenes continued.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

Summary results of alkynes.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	Propyne	29.42932	29.40432	-0.00085
C_4H_6	1-Butyne	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	41.72765	41.75705	0.00070
C_9H_{16}	1-Nonyne	102.37552	102.35367	-0.00021

Summary results of alcohols.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4O	Methanol	21.11038	21.131	0.00097
C_2H_6O	Ethanol	33.40563	33.428	0.00066
C_3H_8O	1-Propanol	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	69.87873	69.887	0.00011
$C_5H_{12}O$	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	203.61343	203.603	-0.00005

Summary results of ethers.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6O	Dimethyl ether	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
$C_6H_{14}O$	Diisopropyl ether	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	0.00061
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Summary results of 1° amines.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_5N	Methylamine	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	36.04067	36.062	0.00060
C_3H_9N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Summary results of aldehydes.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	Formaldehyde	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	28.18711	28.198	0.00039
C_3H_6O	Propanal	40.34481	40.345	0.00000
C_4H_8O	Butanal	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	101.23420	101.259	0.00025

Summary results of ketones.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6O	Acetone	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	65.00012	64.988	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
$C_9H_{18}O$	2-Nonanone	113.63092	113.632	0.00001
$C_9H_{18}O$	5-Nonanone	113.63092	113.675	0.00039
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Summary results of carboxylic acids.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O_2	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Summary results of carboxylic acid esters.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_4O_2$	Methyl formate	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030

Summary results of carboxylic acid esters continued.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

Summary results of nitriles.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3N	Acetonitrile	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	50.03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C_5H_9N	Pentanenitrile	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Summary results of aromatics and heterocyclic aromatics.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	57.26008	57.26340	0.00006
C_6H_5Cl	Fluorobenzene	57.93510	57.887	-0.00083
C_6H_5Cl	Chlorobenzene	56.55263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	55.84518	55.852	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
$C_6H_3Cl_3$	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C_6Cl_6	Hexachlorobenzene	52.57130	52.477	-0.00179
C_6H_5Br	Bromobenzene	56.17932	56.391[a]	0.00376
C_6H_5I	Iodobenzene	55.25993	55.261	0.00001
$C_6H_5NO_2$	Nitrobenzene	65.18754	65.217	0.00046
C_7H_8	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
$C_7H_5ClO_2$	2-chlorobenzoic acid	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	73.26820	73.261	-0.00010
C_6H_7N	Aniline	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	76.62345	76.654	0.00040

[a] Liquid.

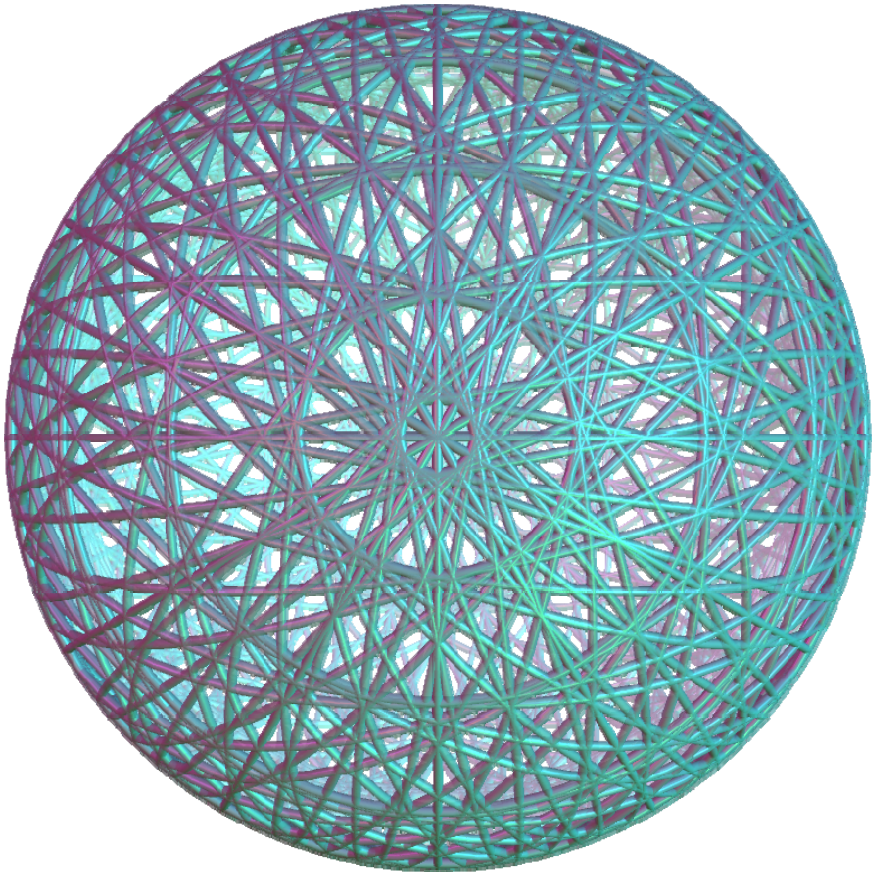
Summary results of aromatics and heterocyclic aromatics continued.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00002
$C_7H_7NO_2$	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
$C_7H_7NO_2$	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C_6H_6O	Phenol	61.75817	61.704	-0.00087
$C_6H_4N_2O_5$	2,4-dinitrophenol	77.61308	77.642	0.00037
C_6H_8O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_8$	Naphthalene	90.74658	90.79143	0.00049
C_4H_5N	Pyrrole	44.81090	44.785	-0.00057
C_4H_4O	Furan	41.67782	41.692	0.00033
C_4H_4S	Thiophene	40.42501	40.430	0.00013
$C_3H_4N_2$	Imidazole	39.76343	39.74106	-0.00056
C_5H_5N	Pyridine	51.91802	51.87927	-0.00075
$C_4H_4N_2$	Pyrimidine	46.57597	46.51794	-0.00125
$C_4H_4N_2$	Pyrazine	46.57597	46.51380	0.00095
C_9H_7N	Quinoline	85.40453	85.48607	0.00178
C_9H_7N	Isoquinoline	85.40453	85.44358	0.00046
C_8H_7N	Indole	78.52215	78.514	-0.00010

Summary results of allotropes of carbon.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_n	Diamond	3.74829	3.704	-0.01
C_{60}	Fullerene	419.75539	419.73367	-0.00005
C_n	Graphite	4.91359	4.89866	-0.00305

Theoretical Modeling

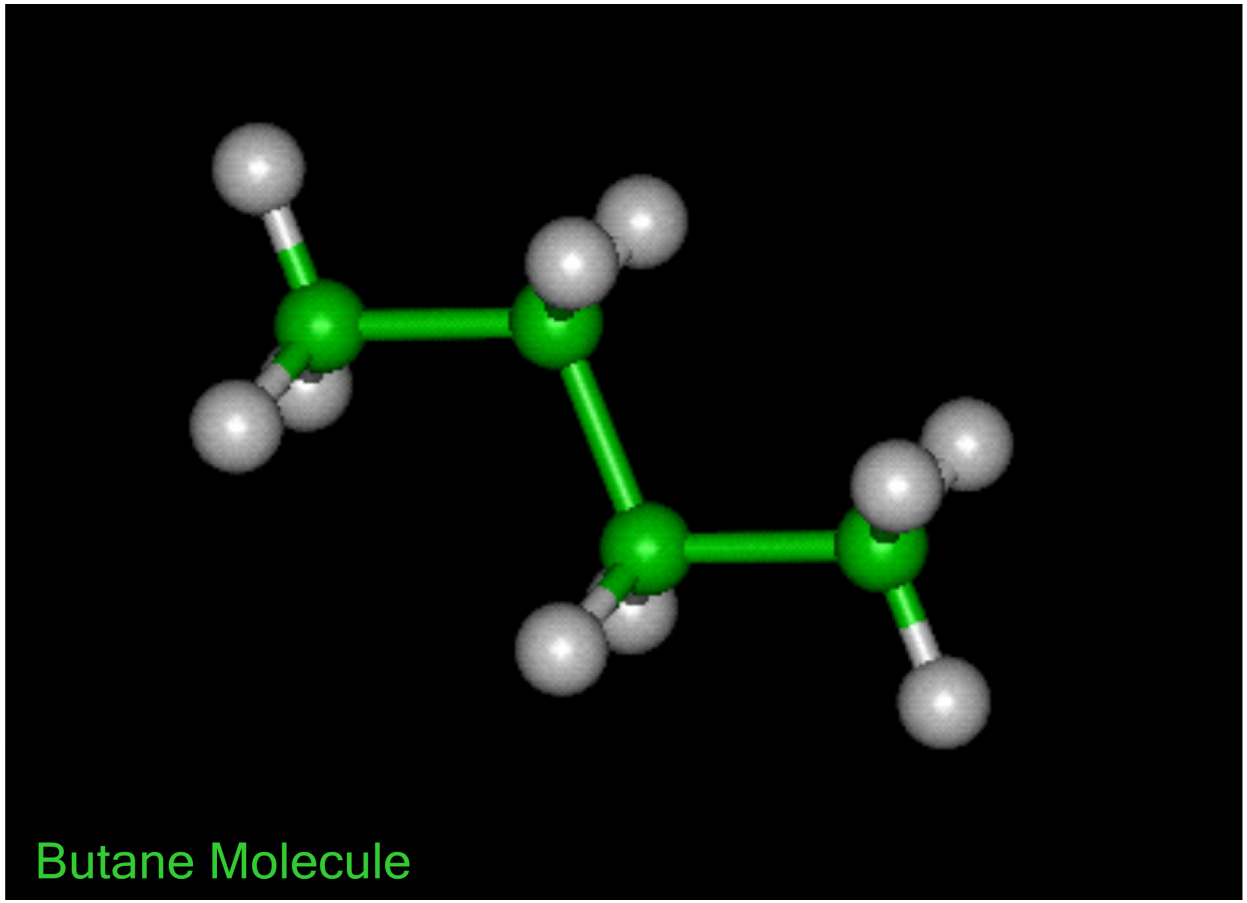


THEORY PRODUCT:
Molecular Modeling Software

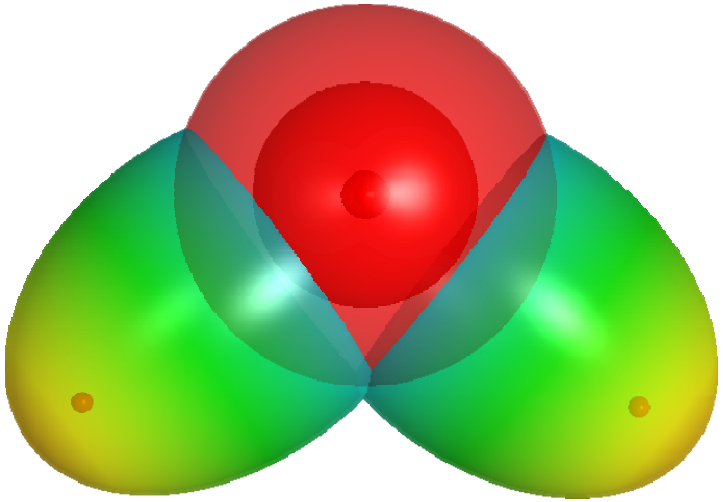
- General: opportunity to improve processes, discover new molecules, new synthetic pathways, new materials, and find new properties and applications for known molecules

- For Pharma: exact solutions can facilitate drug design, identify active structures, predict optimal synthetic pathways, products, and yields

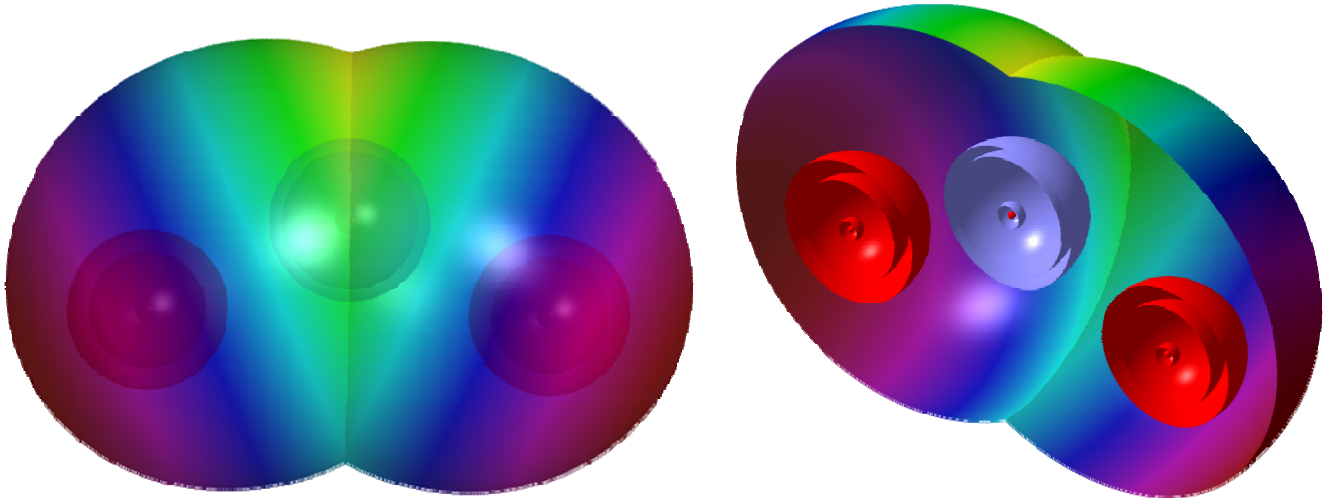
Molecular Structure



Water

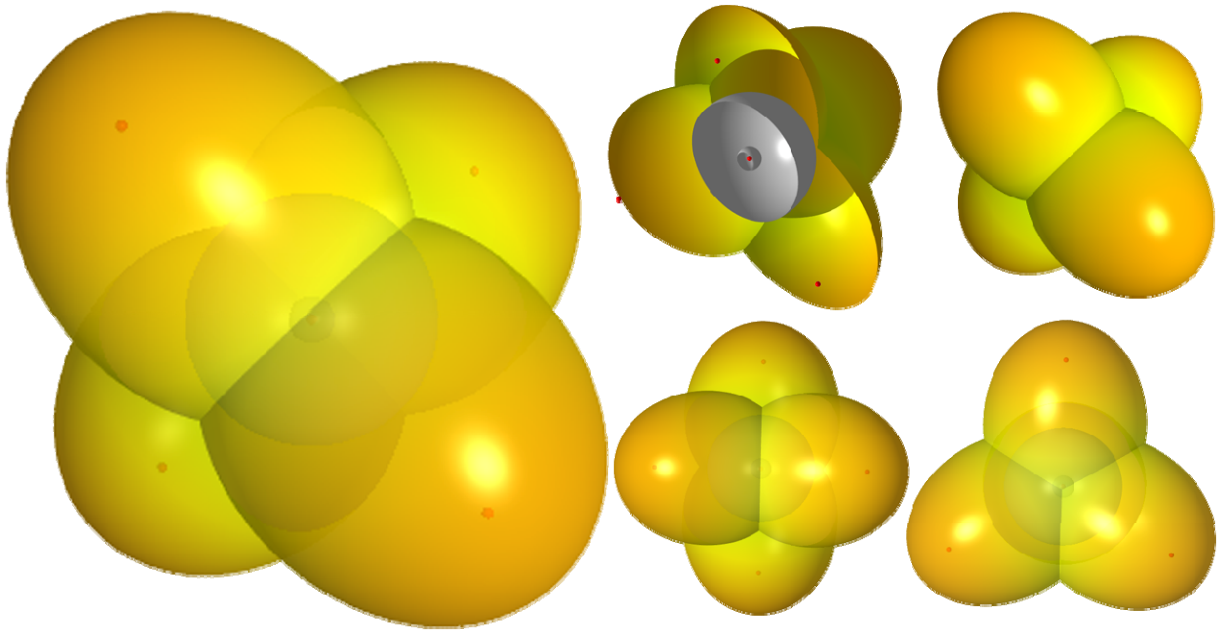


Nitrogen Dioxide

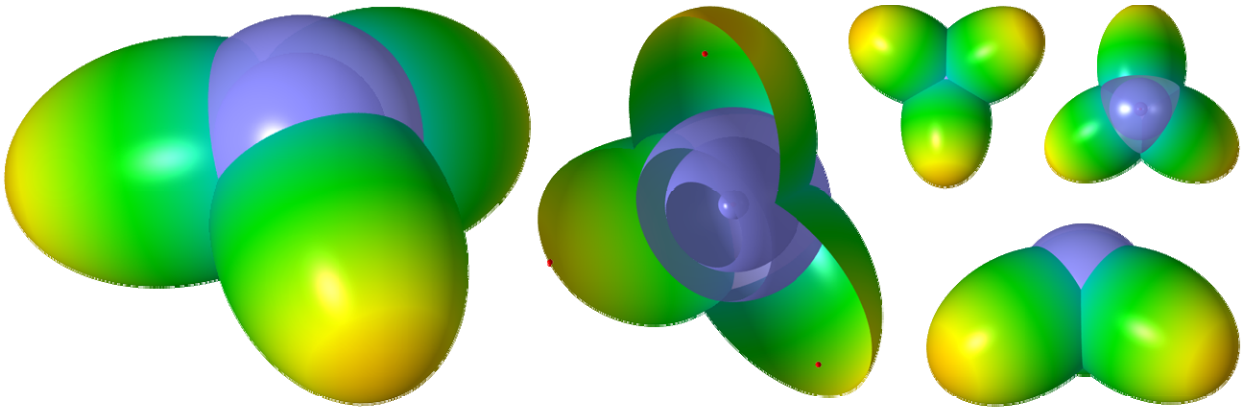




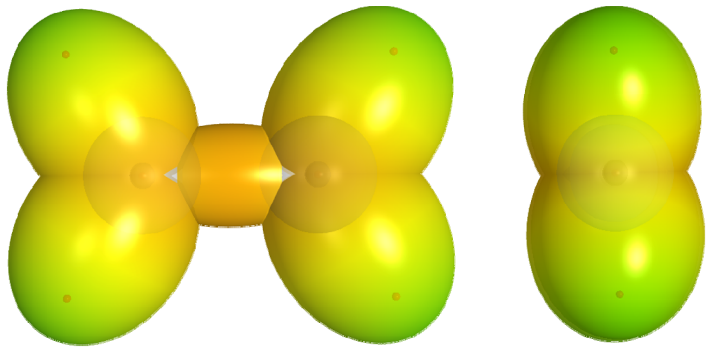
Methane



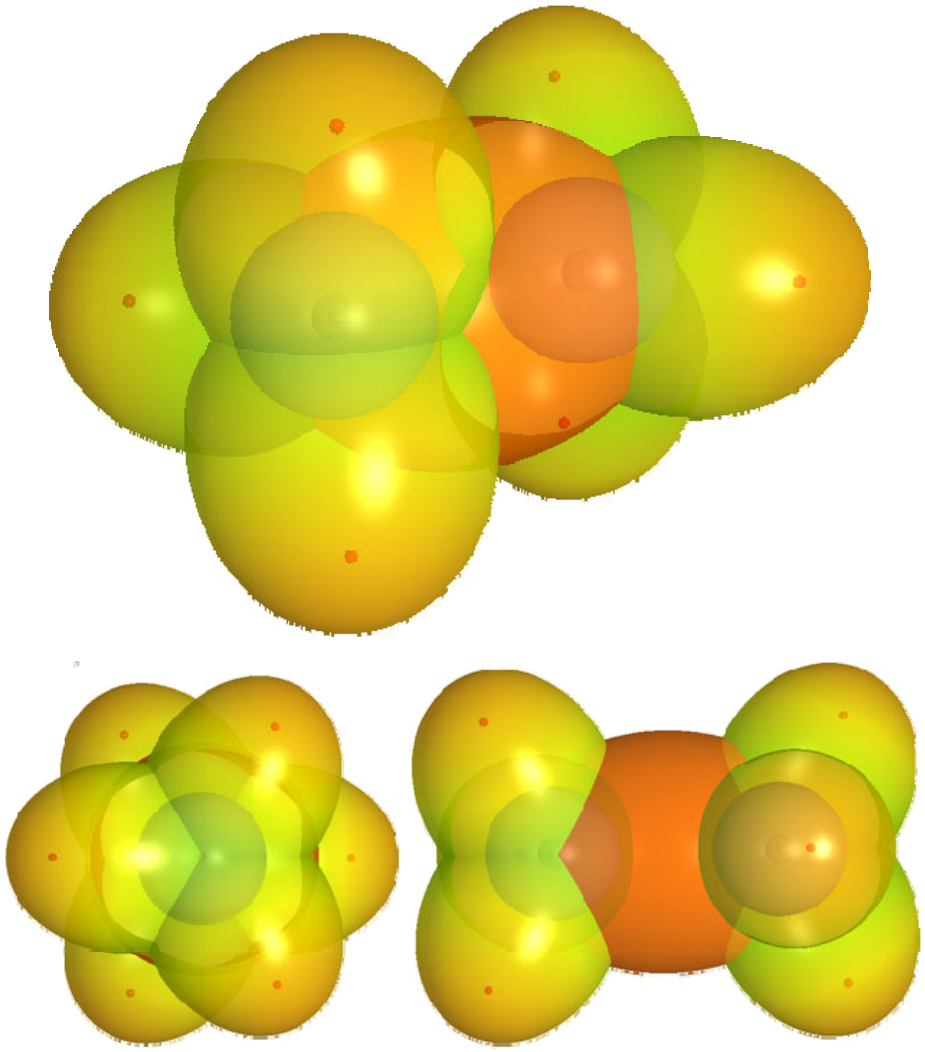
Ammonia







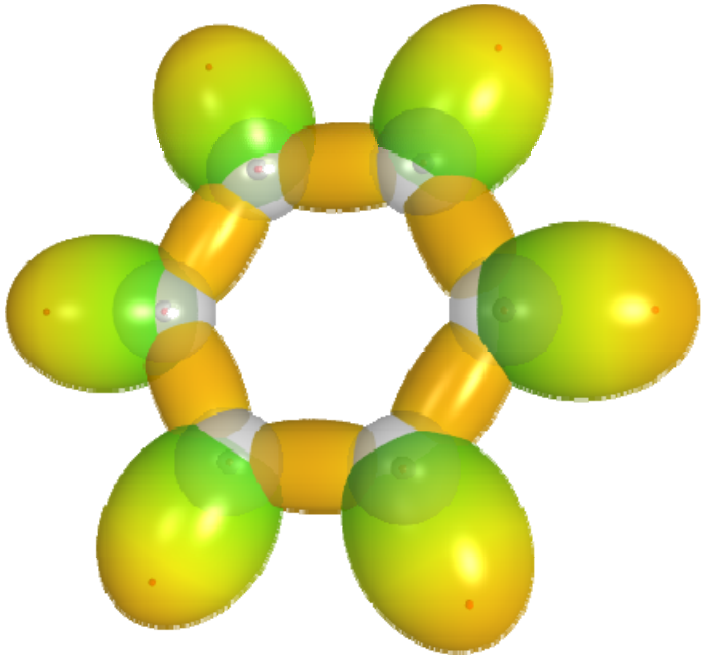
Ethylene



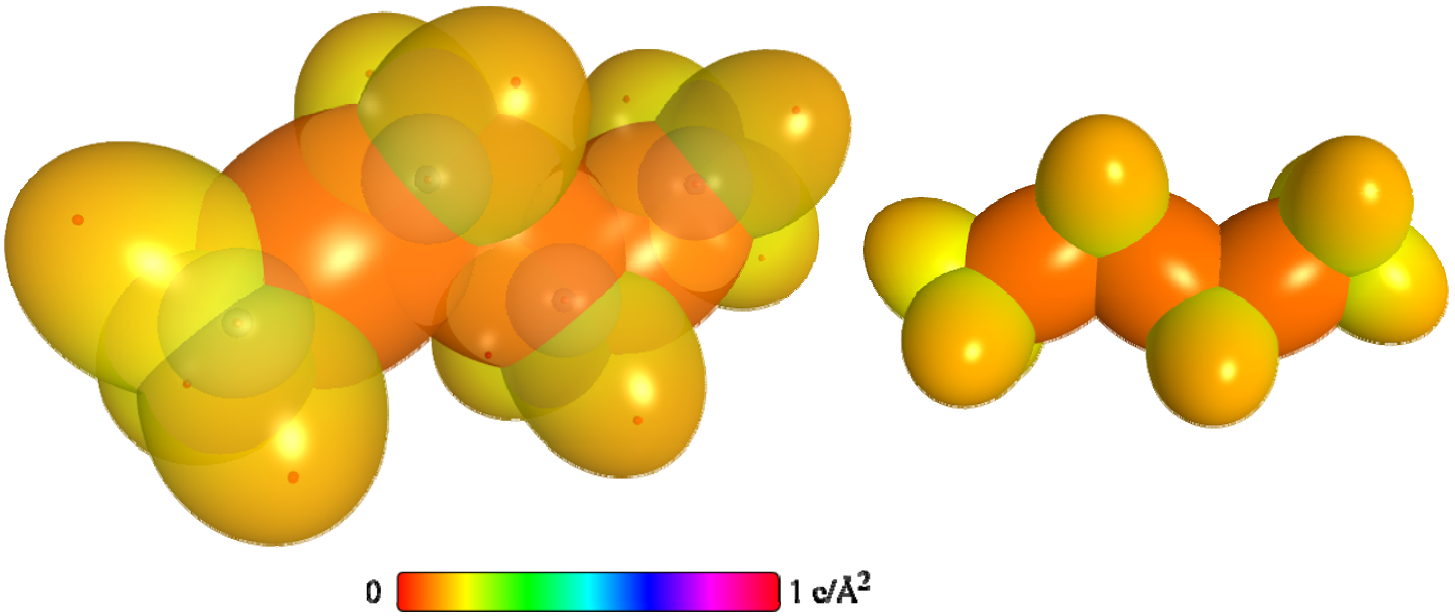
Ethane



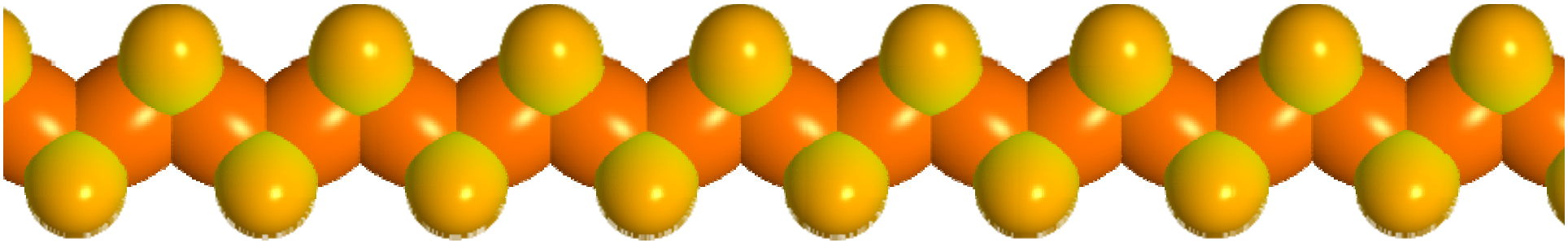
Benzene



Butane

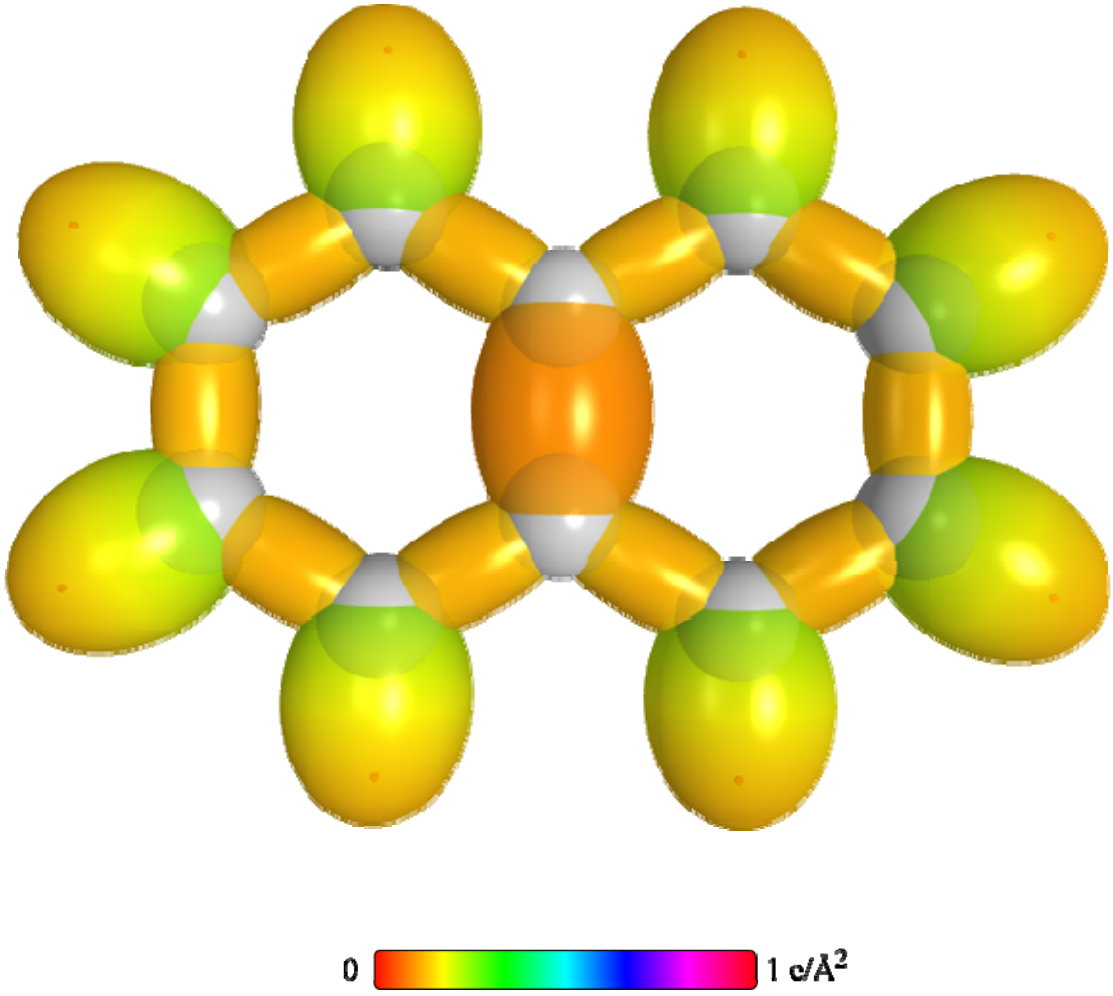


Infinite Length Hydrocarbons

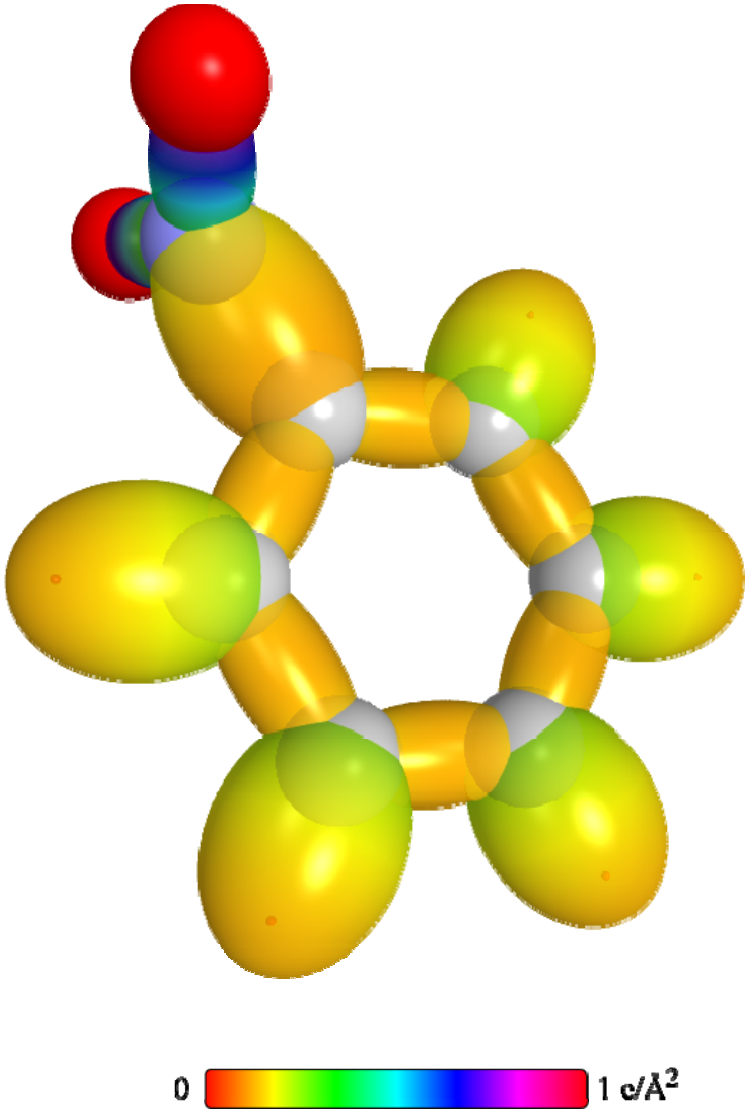




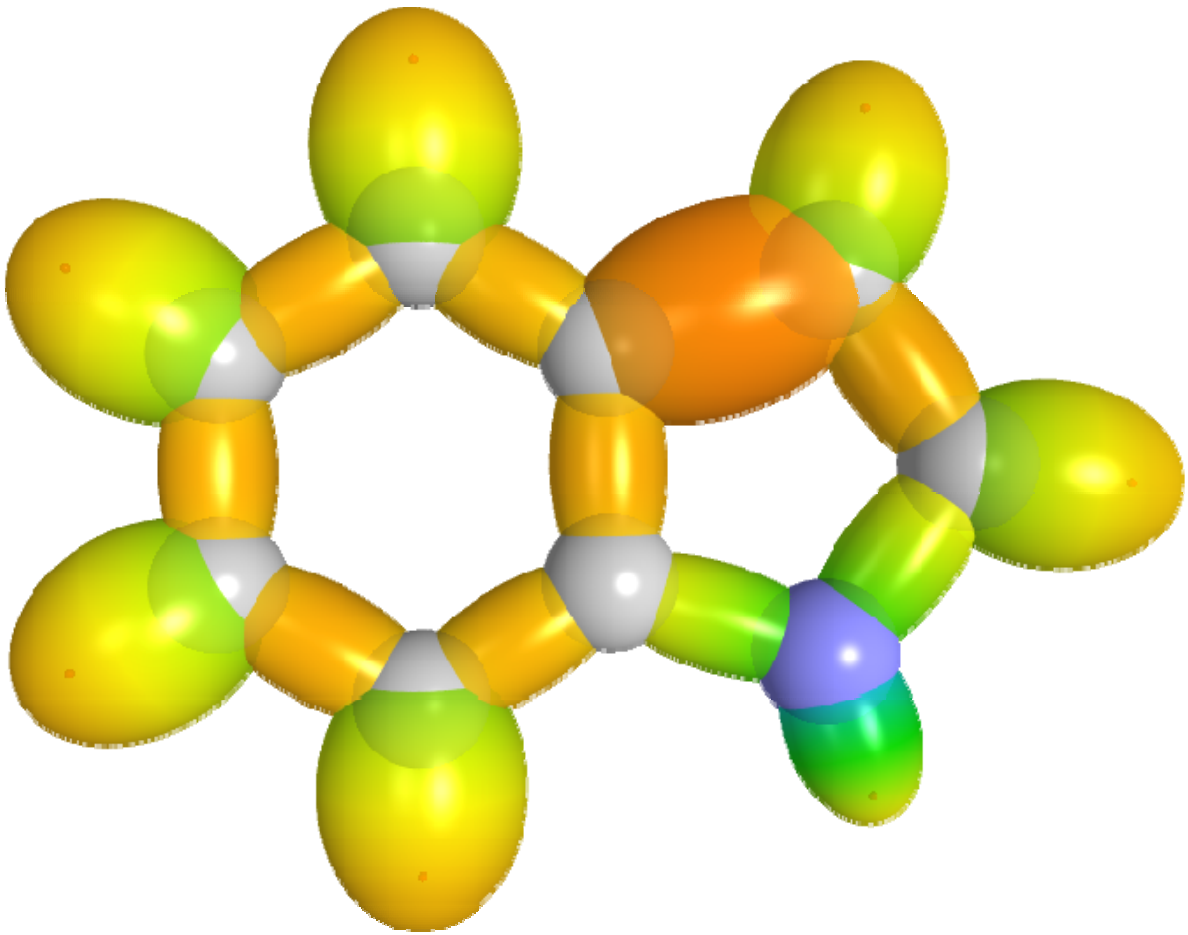
Naphthalene



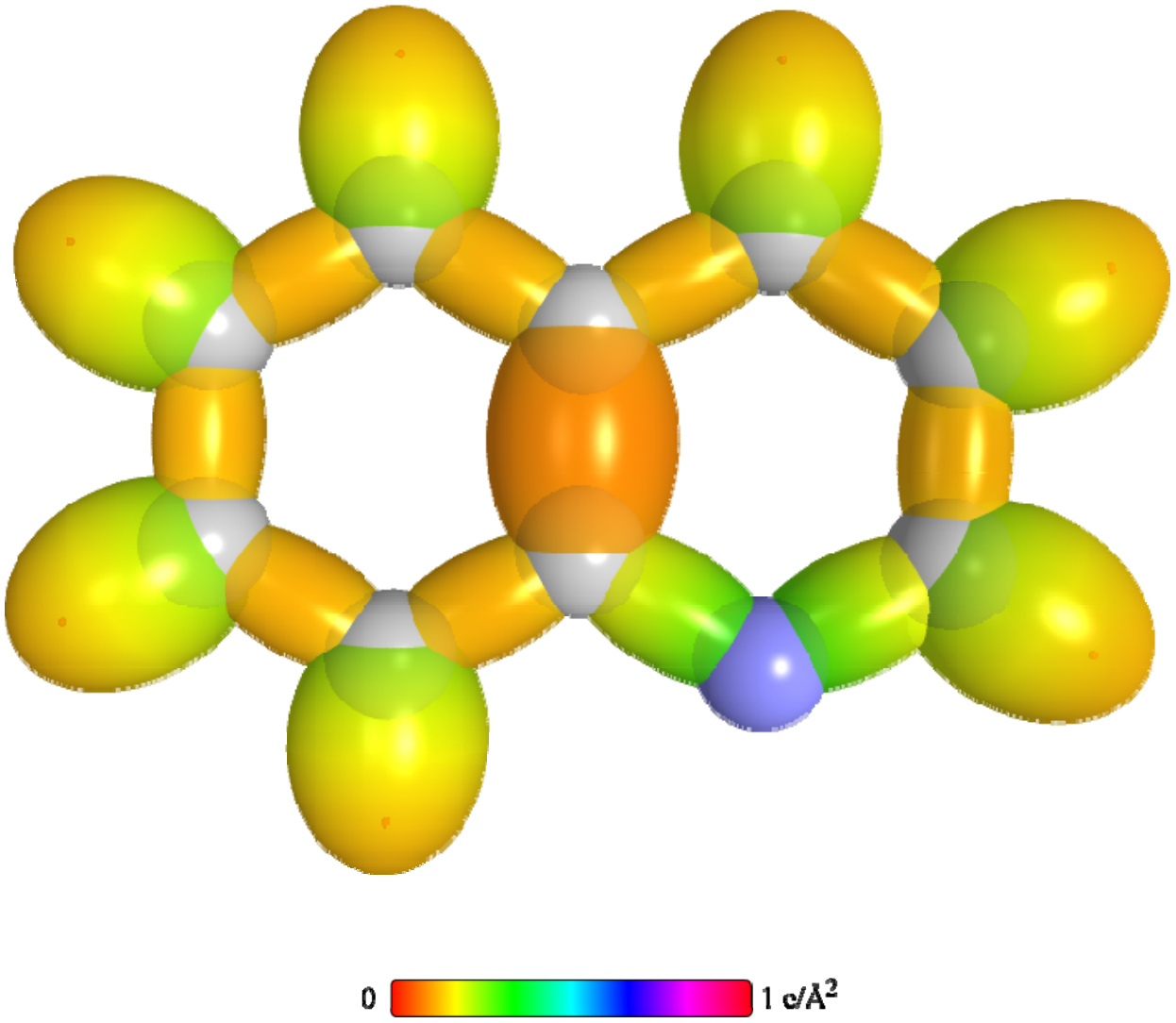
Nitrobenzene



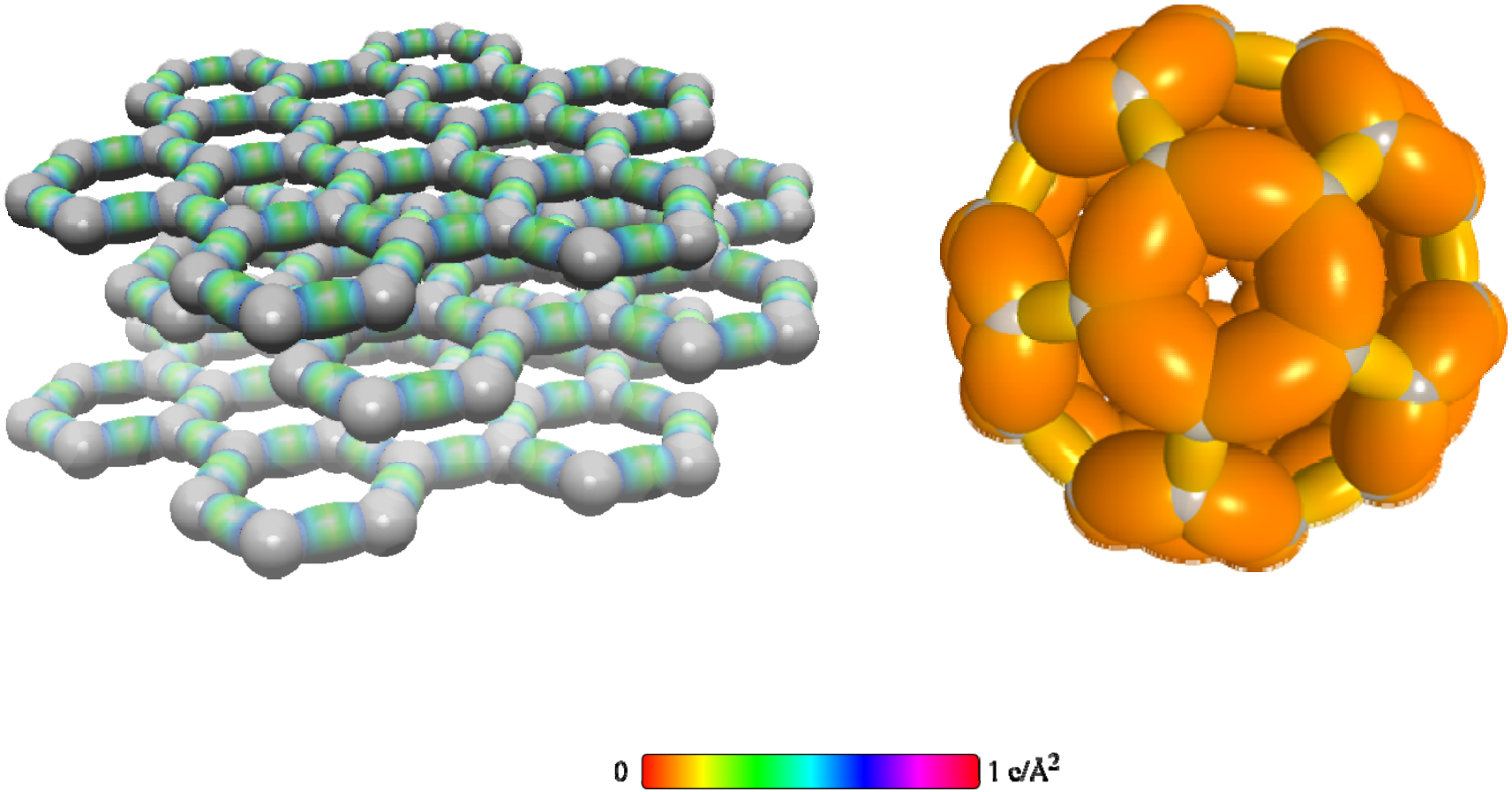
Indole



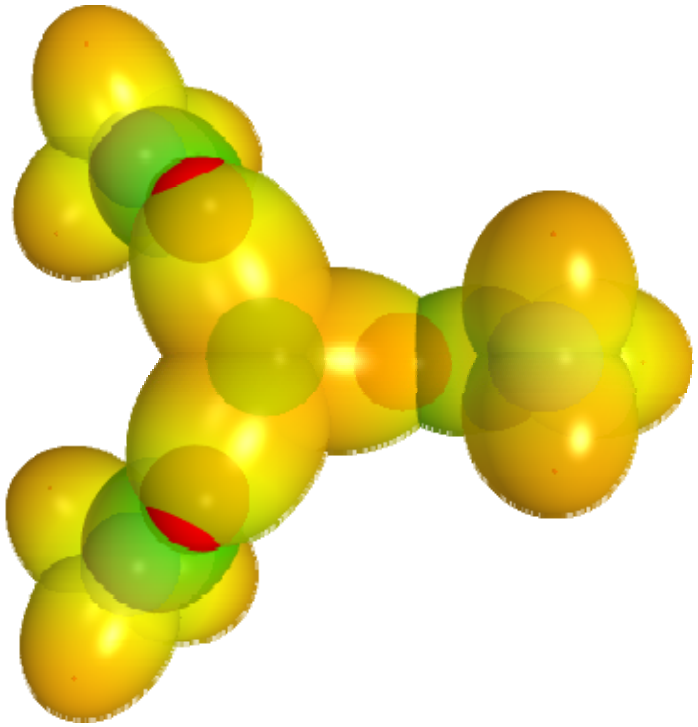
Quinolene



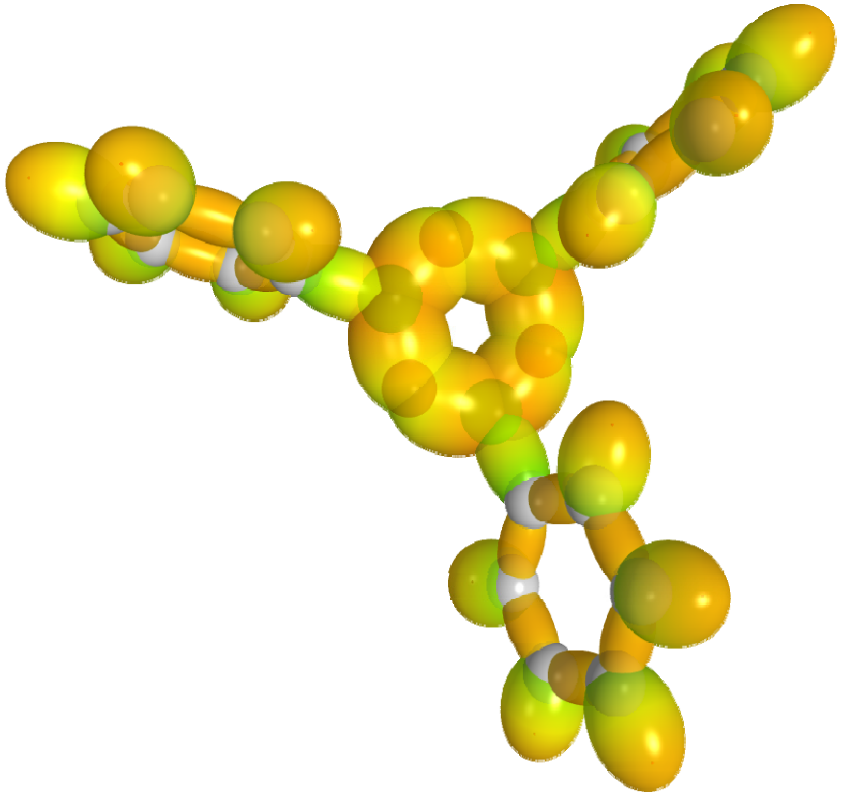
Allotropes of Carbon



Boron: Boranes and Borinic Acids



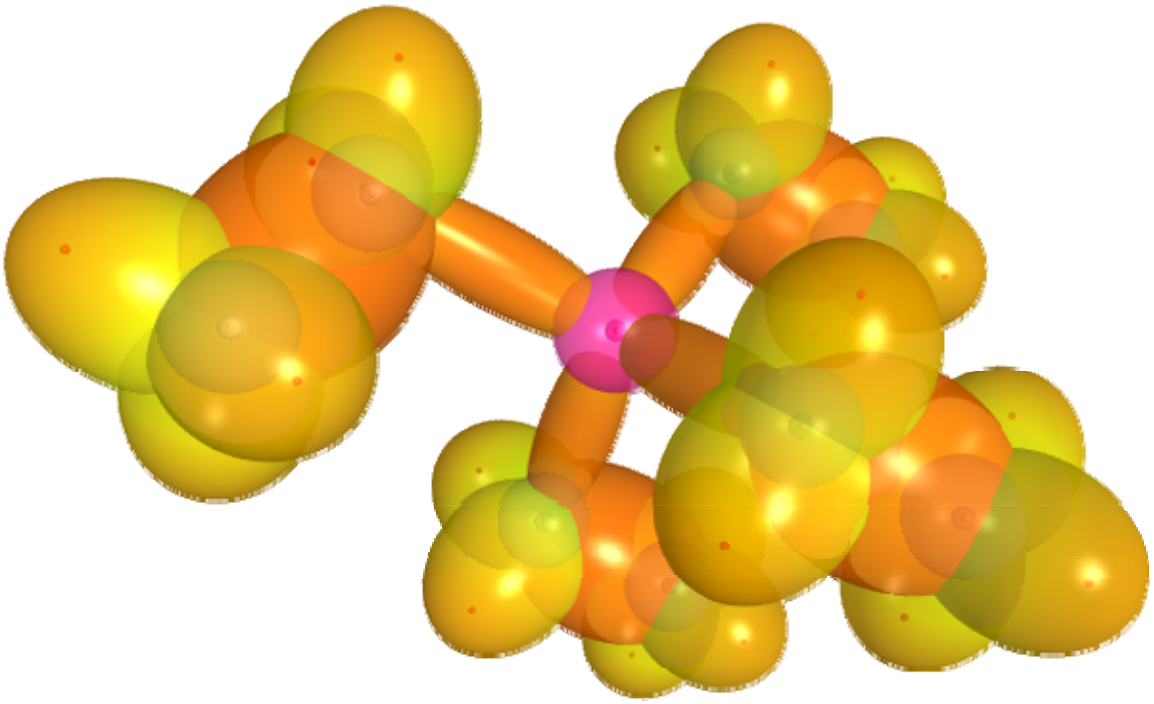
Trimethyloxyborane



Phenylborinic anhydride

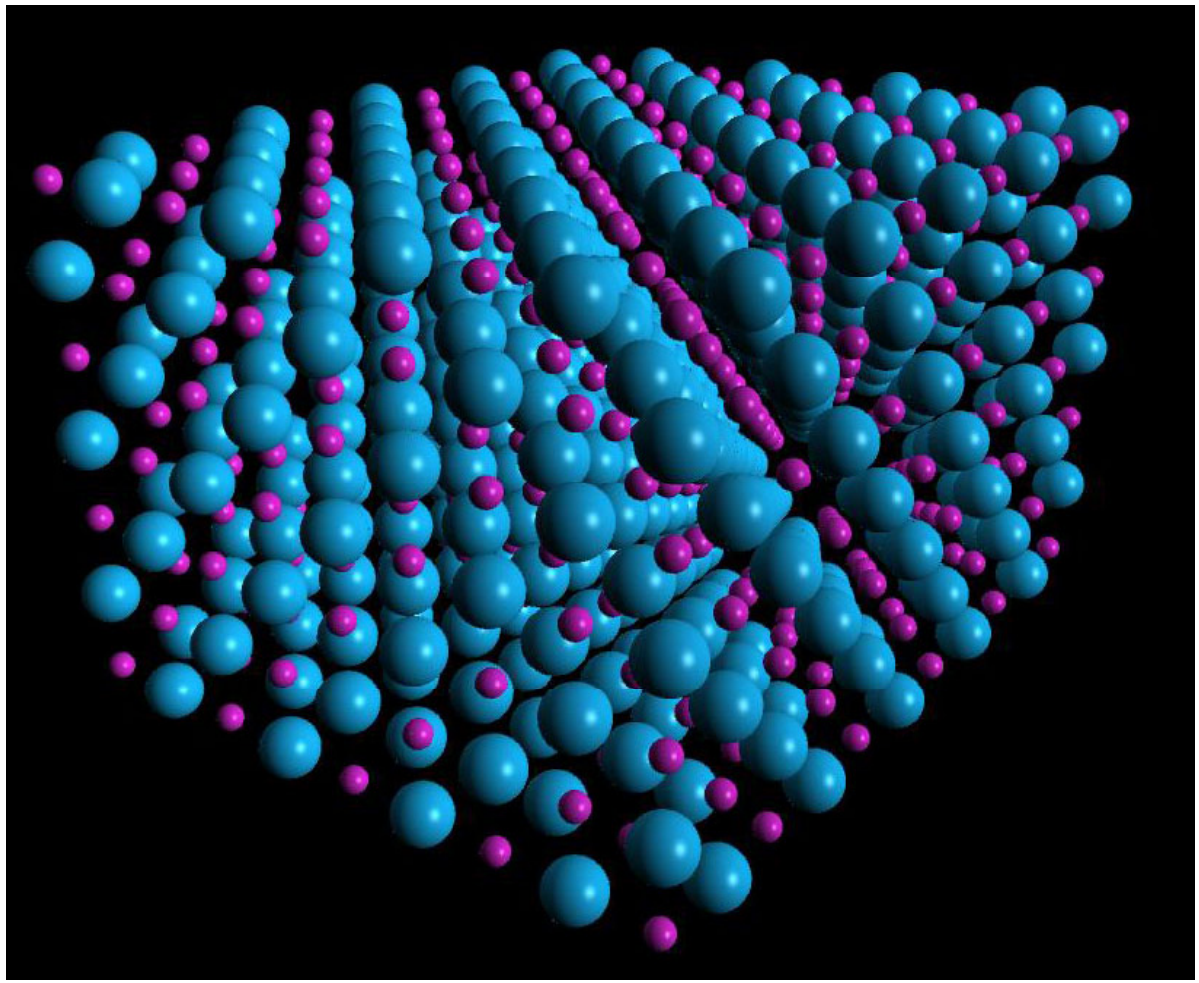


Organometallics:
Tetraethyl-lead

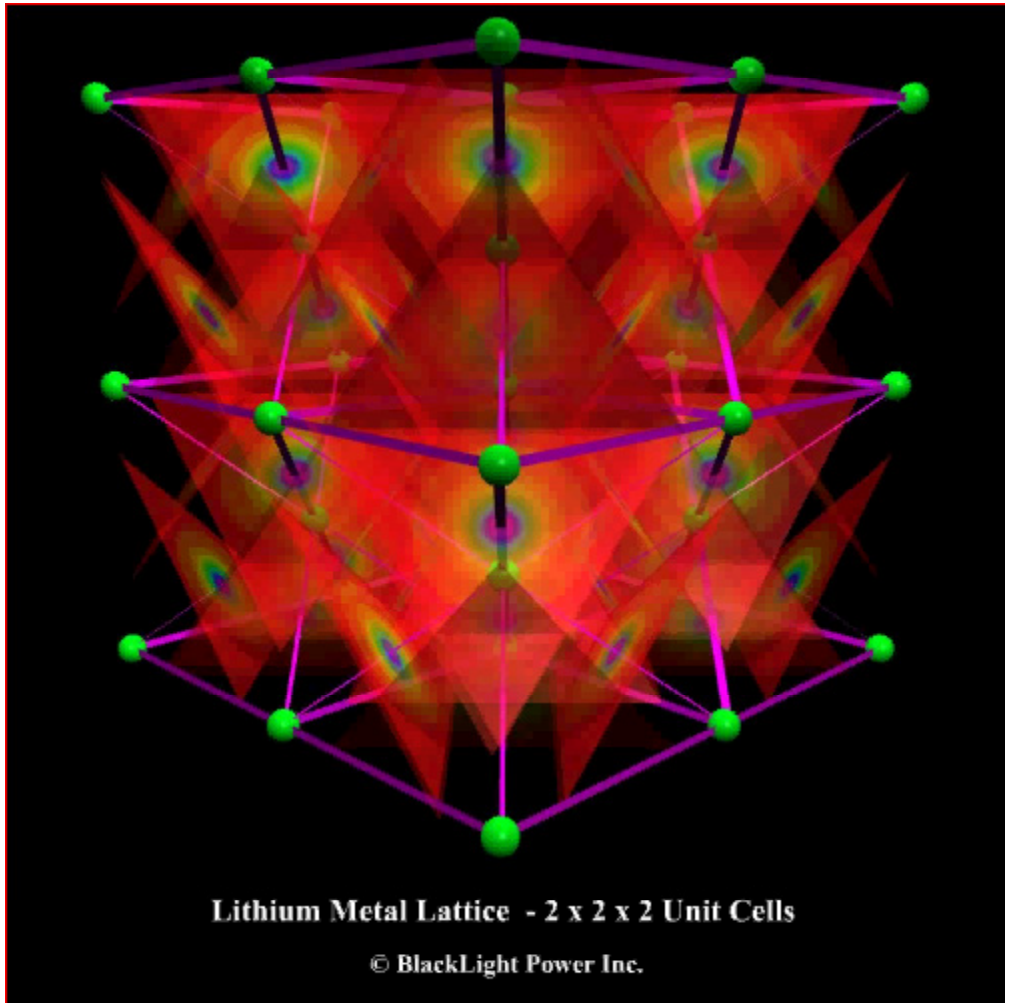




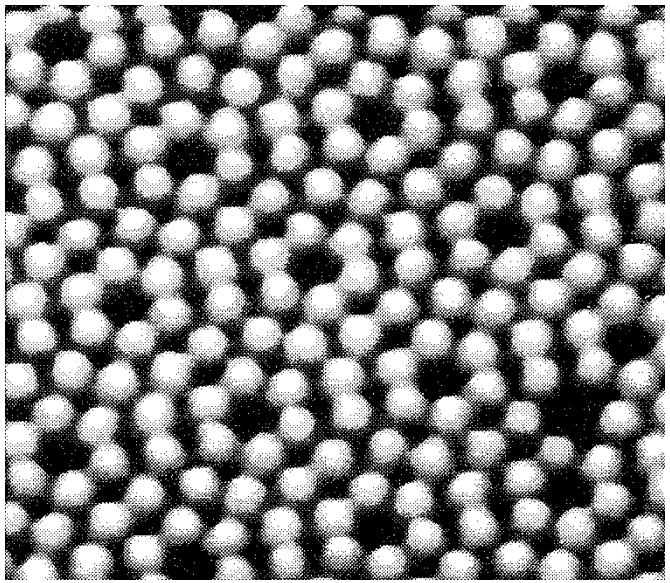
Metal Hydrides

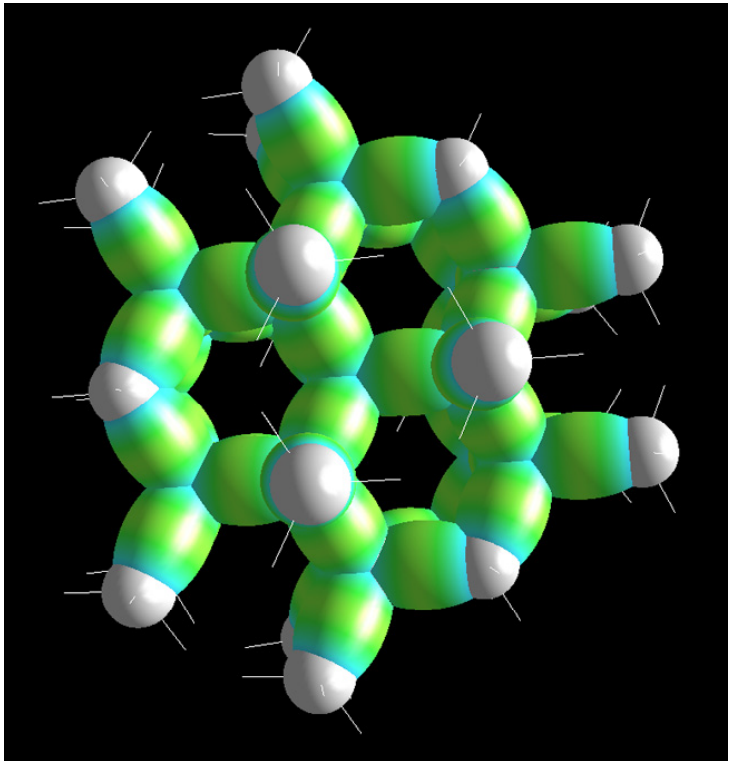


Metals

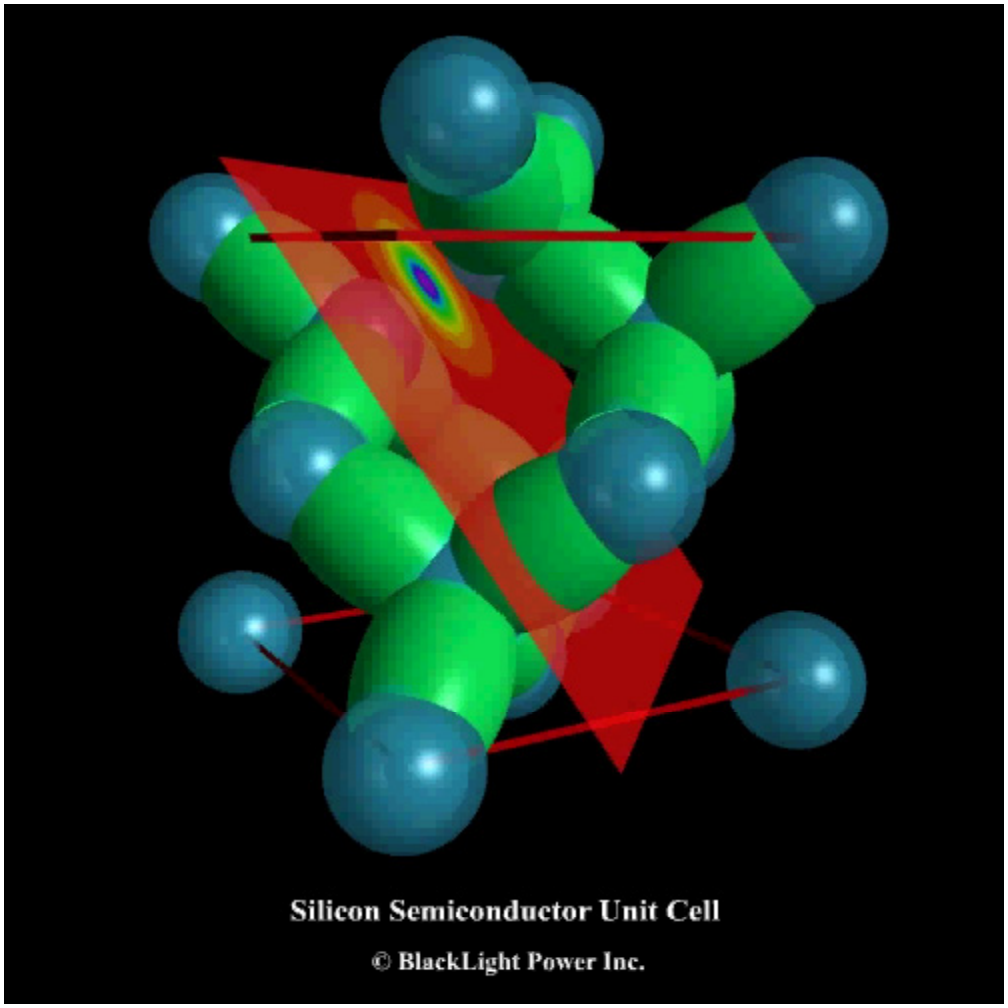

Lithium Metal Lattice - 2 x 2 x 2 Unit Cells
© BlackLight Power Inc.

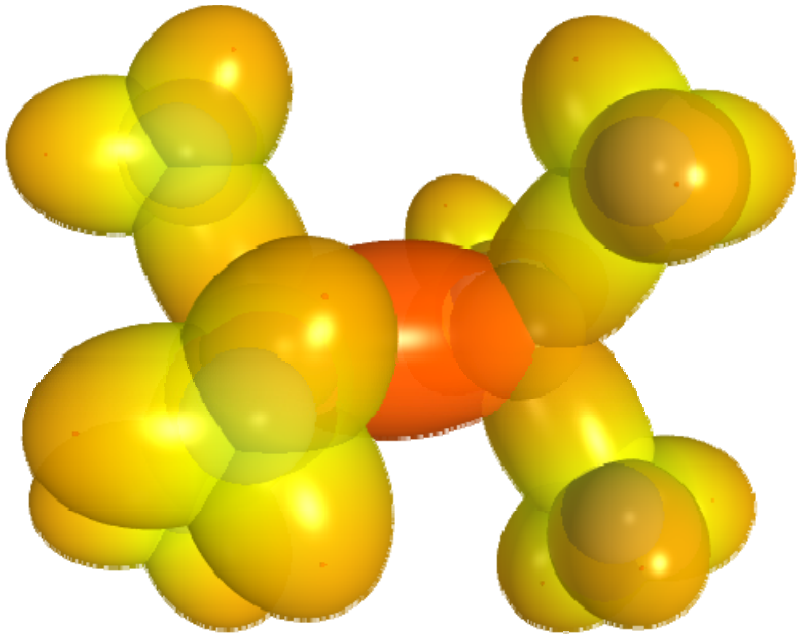
Silicon Structure and Model





Semiconductor and Alkyl silanes

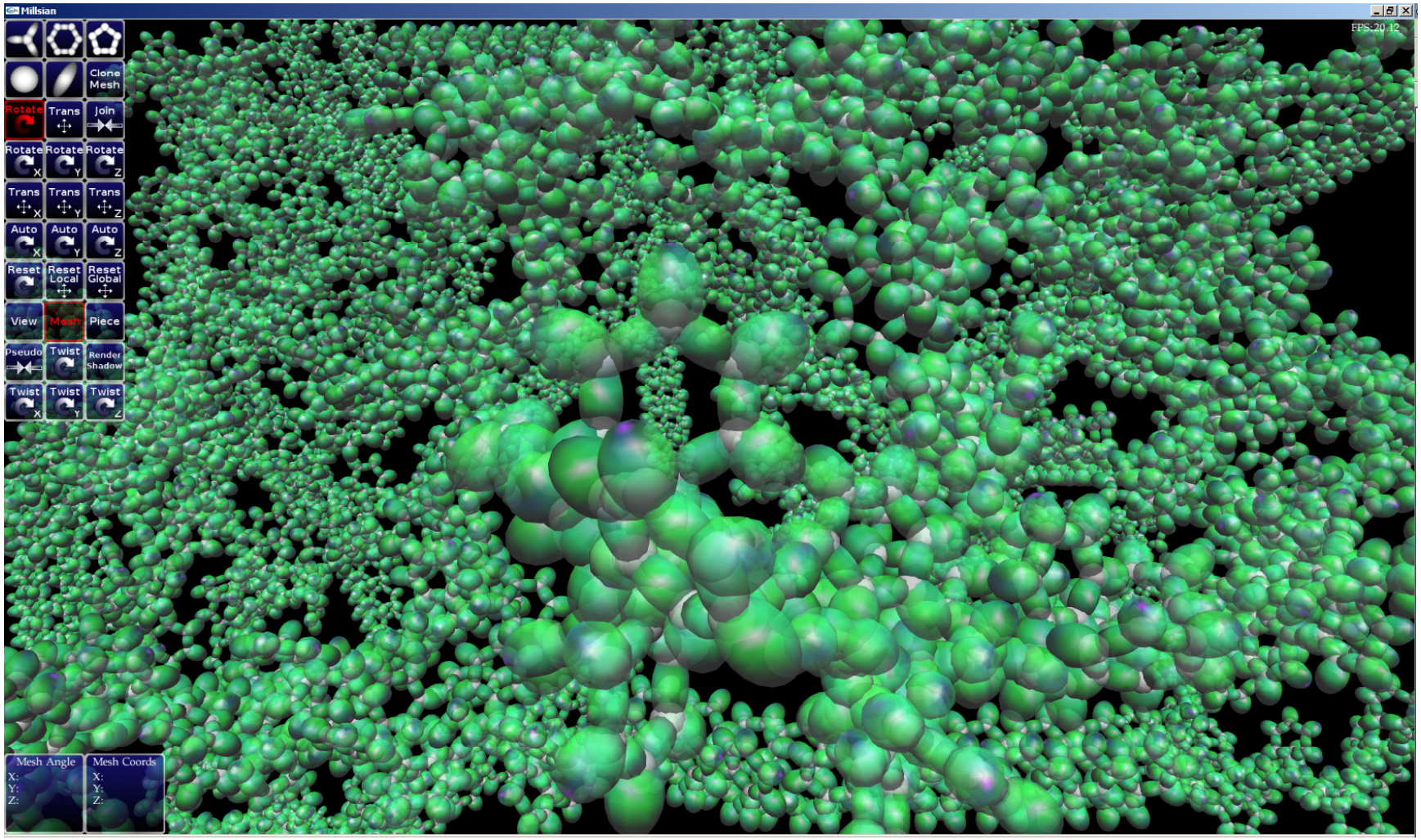






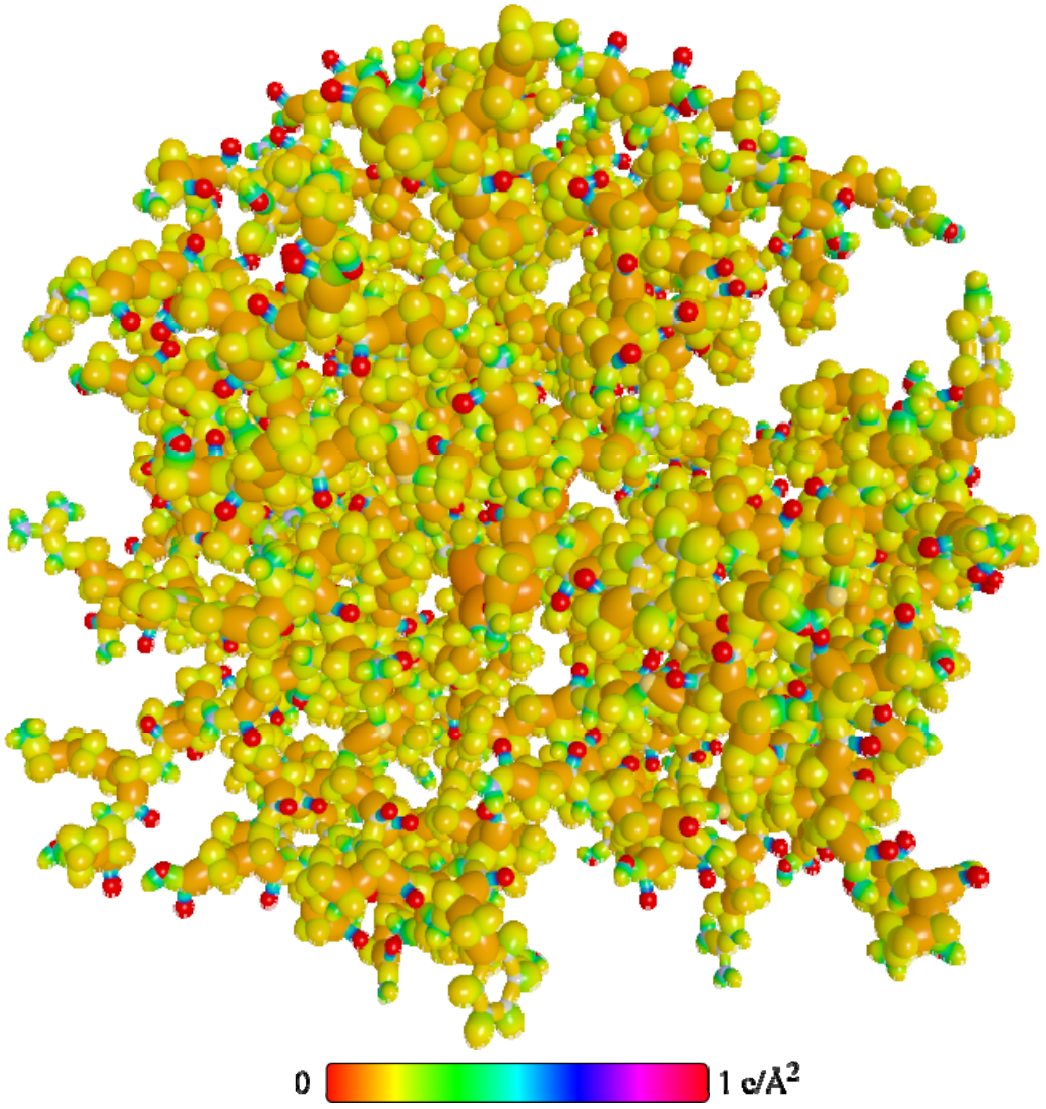
Polymers

Polystyrene

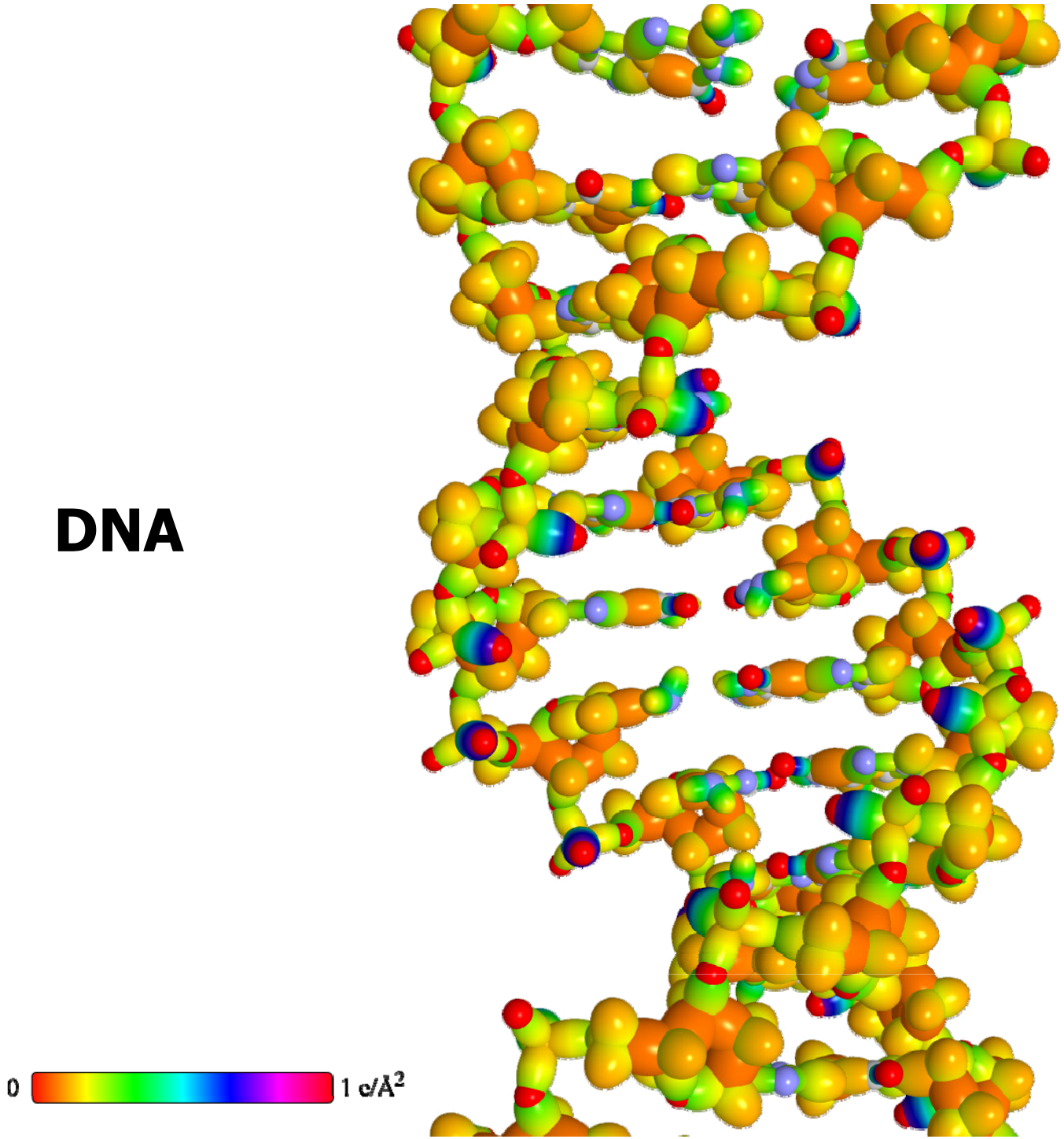


Proteins

Color scale, translucent view of the charge density of insulin created and modeled using Millsian 2.0 using a PC.

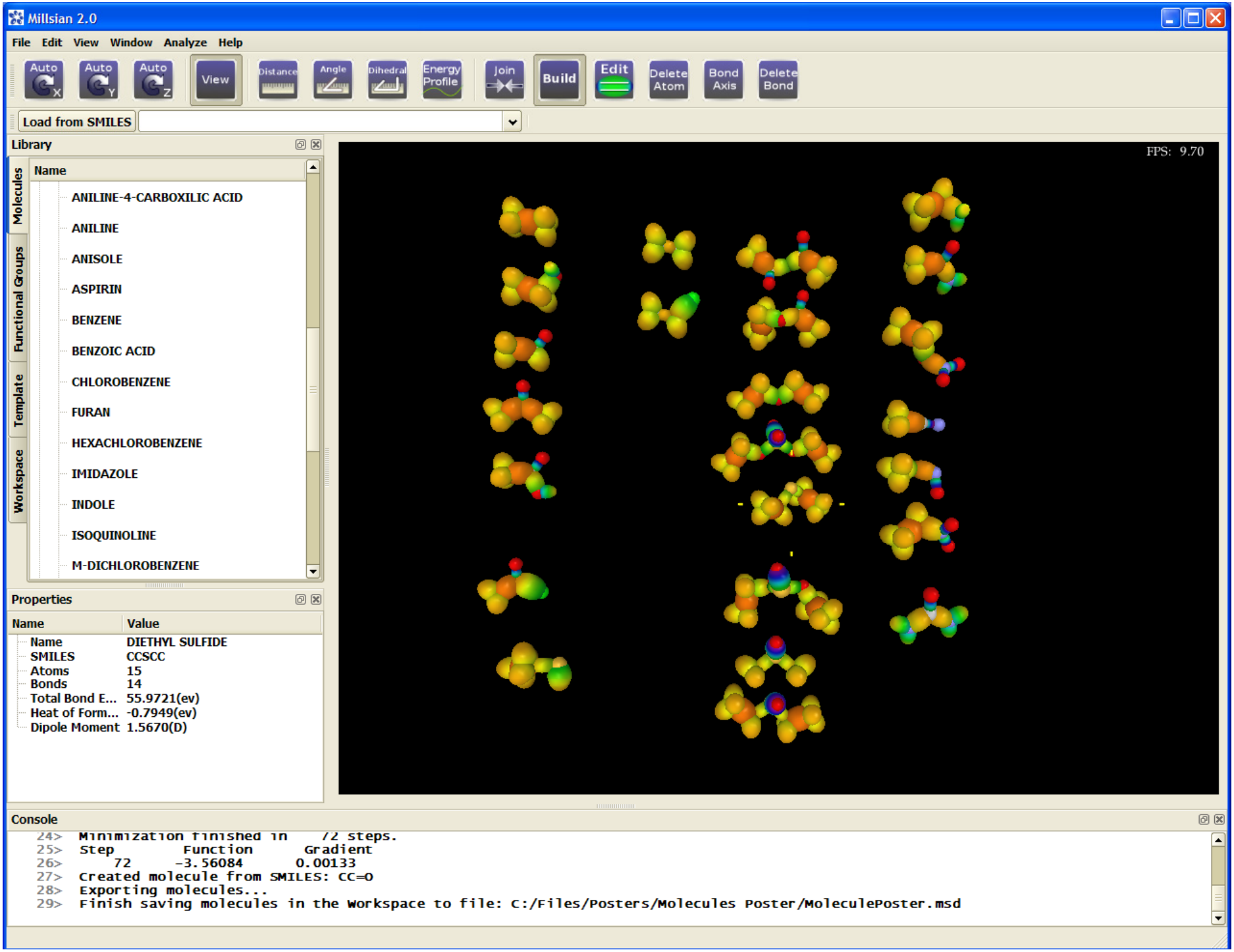


DNA



Outputs and Potential Applications

- Geometric parameters and structure (bond distances, bond angles, molecular orbital axes, radius of each atomic orbital)
  - Measuring sticks for arbitrary points on molecule
  - Cross sections for collisions with other particles and reactivity
  - Shadow feature that allows molecules to be superimposed and compared for differences and similarities to find regions of biological activity
- Charge densities of all atomic and molecular orbitals
  - Predict reactivity
  - Calculate dipoles and higher multipole moments
  - Parameters to calculate fields, interactions, and physical properties
  - Parameters to solve field interaction for lowest energy conformation, dynamics, refractive index, melting and boiling points
- Component energies of all atomic and molecular orbitals (potential energy, kinetic energy, nuclear repulsive energy, magnetic potential energy)
  - Predict reactivity
  - Parameters for Lagrangian to solve for vibrational and rotational levels and IR spectrum
  - Other spectroscopic quantities
  - Calculate thermodynamic parameters of entropy and heat capacity
  - Use enthalpies to calculate kinetics and equilibrium constants
- Other General Applications to Outputs
  - Calculate the topography of a drug site based on drug structure-activity profile
  - Point and click feature for charge density, bond energy, component energies, distance parameters
  - Fit a site application-identify the ideal molecule to fit a 3-dimensional topography (enzymatic site)
  - Chemistry simulations and reaction dynamics
  - Protein folding problem
  - DNA and RNA structure


Millsian 2.0
File Edit View Window Analyze Help
Auto X
Auto Y
Auto Z
View
Distance
Angle
Dihedral
Energy Profile
Join
Build
Edit
Delete Atom
Bond Axis
Delete Bond
Load from SMILES
Library
Molecules
Functional Groups
Template
Workspace
Name
ANILINE-4-CARBOXILIC ACID
ANILINE
ANISOLE
ASPIRIN
BENZENE
BENZOIC ACID
CHLOROBENZENE
FURAN
HEXACHLOROBENZENE
IMIDAZOLE
INDOLE
ISOQUINOLINE
M-DICHLOROBENZENE
FPS: 9.70
Properties
Name Value
Name DIETHYL SULFIDE
SMILES CCSCC
Atoms 15
Bonds 14
Total Bond E... 55.9721(ev)
Heat of Form... -0.7949(ev)
Dipole Moment 1.5670(D)
Console
24> Minimization finished in 72 steps.
25> Step Function Gradient
26> 72 -3.56084 0.00133
27> Created molecule from SMILES: CC=O
28> Exporting molecules...
29> Finish saving molecules in the Workspace to file: C:/Files/Posters/Molecules Poster/MoleculePoster.msd

Bond and Dipole Moments

- The charge of each functional group must redistribute between the different spherical orbitals of the bonding atoms to achieve a corresponding current-density that maintains constant current at the equivalent-energy condition according to the energy-matching factor.
- Since the orbital energy and radius are reciprocally related, the contribution scales as the square of the ratio (over unity) of the energy of the resultant net positively-charged orbital and the initial matched energy of the resultant net negatively-charged orbital of the bond multiplied by the energy-matching factor.
- The partial charges on the HOs or AOs corresponding to the charge contribution are equivalent to point charges centered on the nuclei.

Bond and Dipole Moments cont'd

- Due to symmetry, the bond moment μ of each functional group is along the internuclear axis and is calculated from the partial changes at the separation distance, the internuclear distance.
- The bond moment μ along the internuclear axis of *A* – *B* due to the partial charge *q* on each atom is given by

$$\mu = qd = n_1 ce\left(1 - \left(\frac{E_A(valence)}{E_B(valence)}\right)^2\right)2c'$$

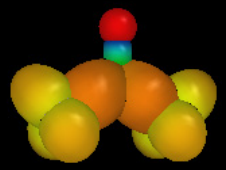
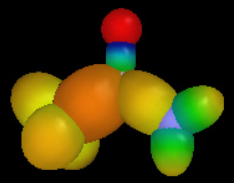
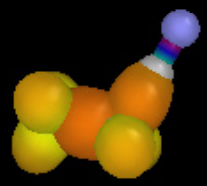
wherein *A* and *B* are the net positively and negatively-charged atoms, respectively, n_1 is the number of equivalent bonds of the MO, *c* is energy-matching factor, *d* is the charge-separation distance, the internuclear distance 2*c*', $E_B(valence)$ is the initial matched energy of the resultant net negatively-charged orbital of the bond that is further lowered by bonding to atom *A* having an energy $E_A(valence)$.

Bond and Dipole Moments cont'd

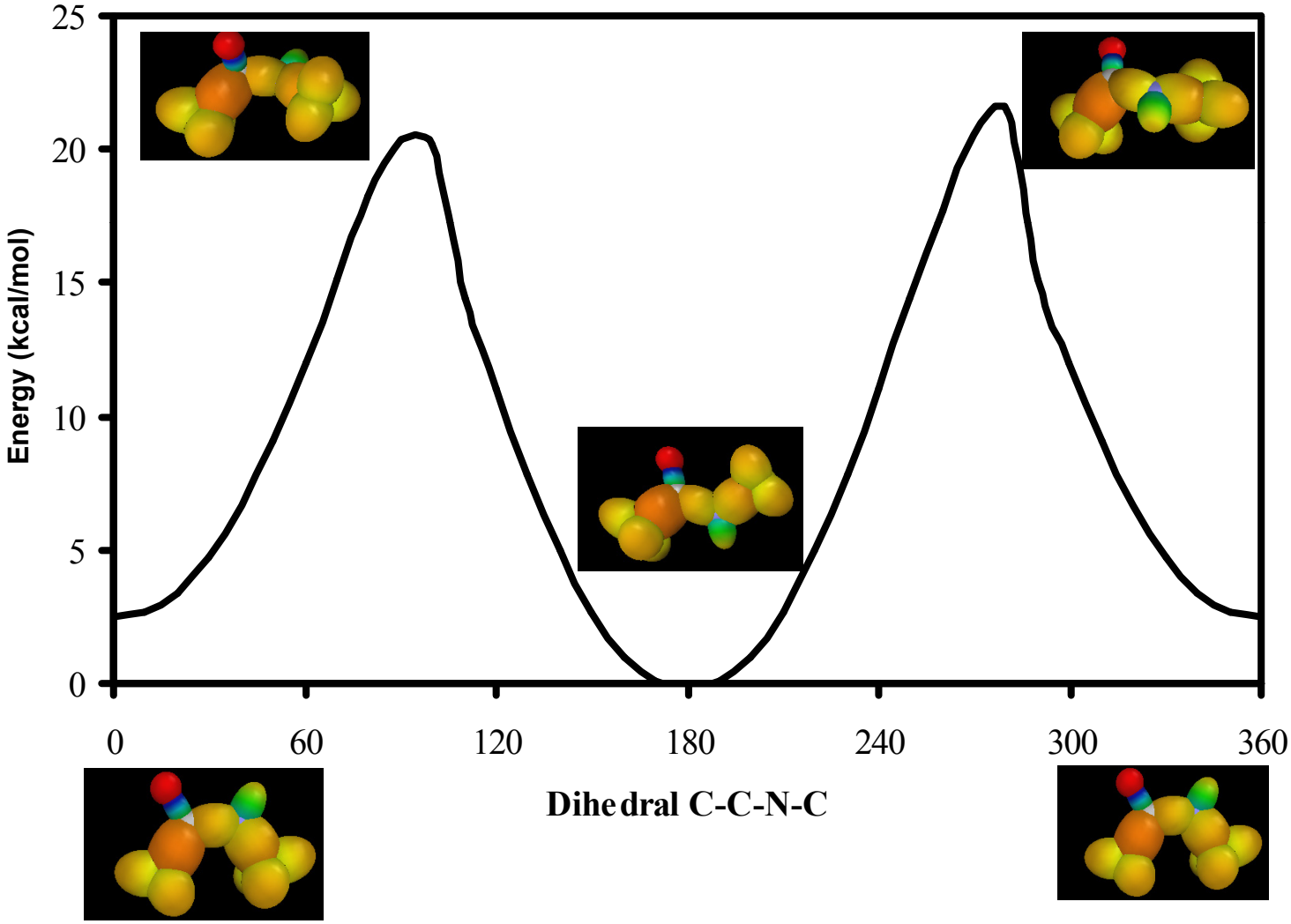
The bond moments of functional groups compared to experimental values wherein the parameters correspond to those of the corresponding functional group.

Functional Group [a]	n_1	$(c_1)c_2$	$(C_1)C_2$	$E_B(valence)$	$E_A(valence)$	$\frac{q}{e}$	Bond Length $2c'$ $(\AA)$	Bond Moment μ (D)	Exp. Bond Moment μ (D)
$H-C$ (alkyl)	1	0.91771	1	14.63489	15.35946	0.070	1.11713	0.37	0.4
$H-C$ (aromatic)	1	0.91771	1	15.95955	15.95955	0	1.09327	0	0
$H-N$ [b] (amine)	1	0.78896	1	13.59844	15.81768	0.279	1.00343	1.34	1.31
$H-N$ [c] (ammonia)	1	0.74230	1	13.59844	15.81768	0.262	1.03677	1.30	1.31
$H-O$ [d] (alcohol)	1	0.91771	1	13.59844	15.81768	0.324	0.97165	1.51	1.51
$H-O$ [e] (water)	1	0.91419	1	13.59844	15.81768	0.323	0.97157	1.51	1.51
$C-N$	1	0.91140	1	14.53414	14.82575	0.037	1.46910	0.26	0.22
$C-O$	1	0.85395	1	14.63489	15.56407	0.112	1.41303	0.76	0.74
$C-F$ [f]	1	1.09254[b]	1	14.63489	15.98435	0.211	1.38858	1.41	1.41
$C-Cl$	1	1	(2)0.81317	14.63489	15.35946	0.165	1.79005	1.42	1.46
$C-Br$	1	1	(2)0.74081	14.63489	15.35946	0.150	1.93381	1.40	1.38
$C-I$ [g]	1	1	(2)0.65537	14.63489	15.28545	0.119	2.13662	1.22	1.19
$C=O$	2	0.85395	1	14.63489	16.20002	0.385	1.20628	2.23	2.3
$C\equiv N$	3	0.91140	1	14.63489	16.20002	0.616	1.16221	3.44	3.5
$H-S$ [h]	1	0.69878	1	14.63489	15.81768	0.118	1.34244	0.76	0.69
$C-S$	1	1	0.91771	14.63489	15.35946	0.093	1.81460	0.81	0.9
$S-O$	1	1	0.77641	14.63489	15.76868	0.125	1.56744	0.94	1.0
$S=O$ [i]	2	0.82897	1	10.36001	11.57099	0.410	1.49118	2.94	2.93
$N-O$	1	1.06727	1	14.53414	14.82575	0.043	1.40582	0.29	0.30
$N=O$ (nitro)	2	0.91140	1	14.63489	15.95955	0.345	1.22157	2.02	2.01
$C-P$	1	1	0.73885	14.63489	15.35946	0.075	1.86534	0.67	0.69
$P-O$	1	0.79401	1	14.63489	15.35946	0.081	1.61423	0.62	0.60
$P=O$ [j]	2	1.25942	1	14.63489	15.76868	0.405	1.46521	2.85	2.825
$Si-H$	1	1	0.75800	10.25487	11.37682	0.131	1.48797	0.94	0.99
$Si-C$	1	1	0.70071	14.63489	15.35946	0.071	1.87675	0.64	0.60
$Si-O$ [l]	1	1	1.32796	10.25487	10.87705	0.166	1.72480	1.38	1.38
$B-H$ [k]	1	1.14361	1	11.80624	12.93364	0.172	1.20235	0.99	1.0
$B-C$	1	0.80672	1	14.63489	15.35946	0.082	1.57443	0.62	0.69
$B-O$ (alkoxy)	1	1	0.79562	11.80624	12.93364	0.159	1.37009	1.05	0.93
$B-N$	1	1	0.81231	11.89724	14.53414	0.400	1.36257	2.62	2.68
$B-F$ [m]	1	0.85447	1	14.88734	17.42282	0.316	1.29621	1.97	1.903
$B-Cl$	1	1	0.91044	11.80624	12.93364	0.182	1.76065	1.54	1.58

Millsian 2.0 Dipole Moment Examples

Molecule	Calculated (D)	Experimental (D)	Error (D)
	1.73	1.69	0.04
	2.82	2.88	-0.06
	3.69	3.68	0.01
	4.09	4.05	0.04

Millsian 2.0 Conformational Energy Example



Nature of the Dipole Bond: Dipole-Dipole, Hydrogen, and van der Waals Bonding

- Since all molecules comprise nuclei that behave on the scale of molecules as electrostatic point charges, and electrically charged electrons exist as charge and current densities that obey Maxwell's equations, the binding is determined by electrical and electrodynamics forces.

- Coulombic-based bonding can be grouped into two main categories:
  - Bonding that comprises permanent dipole-dipole interactions further including an extreme case, *hydrogen bonding*
  - Bonding regarding reversible mutually induced dipole fields in near-neighbor collision-partner molecules called *van der Waals bonding*

Nature of the Dipole Bond: Dipole-Dipole, Hydrogen, and van der Waals Bonding Cont'd

- The H bond is exemplary of the extreme of dipole-dipole interactions as the source of bond energy and rises from the extremely high dipole moments of *H* bound to *F*, *O*, or *N* such that the bond distances are on the order of two angstroms and the energies in the 100's of meV's range.

- For van der Waals bonding, the dipoles are mutually induced rather than permanent, and the mutual induction is small such that the bond distances are on the order of angstroms and the energies in the 10's of meV's range.

Condensed Matter Physics

- The structure and properties of liquids and solids are solved by first solving the unit cell of the condensed solid based on an energy minimum of the molecular interactions and their dependence on the packing.
- Bonding in neutral condensed solids and liquids typically arises from Coulombic interactions between partial charges corresponding to dipoles of the molecules.
- The energy from the interaction of the partial charges increases as the separation decreases, but concomitantly, the energy of a bond that may form between the interacting species increases as well.

Condensed Matter Physics cont'd

- The equilibrium separation distance corresponds to the occurrence of the balance between the Coulombic potential energy of the interacting atoms and the energy of the nascent bond whose formation involves the interacting atoms.

- Thus, the balance is at the energy threshold for the formation of a nascent bond that would replace the interacting partial charges while also destabilizing the standard bonds of the interacting molecules.

Condensed Matter Physics cont'd

The general equation for the balance of the Coulombic energy and the nascent bond energy is given by:

$$\frac{-\delta^+\delta^- e^2}{4\pi\varepsilon_0 r_e} = \left[\left(-\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}}\right]+n_1\frac{1}{2}\hbar\sqrt{\frac{\frac{c_1c_2e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\right]$$

- δ^+ and δ^- are the partial charges of H-bonding atoms
- r_e is the internuclear separation distance of the H-bonded atoms
- n_1 is the number of equivalent bonds of the MO
- c_1 is the fraction of the H_2-type ellipsoidal MO basis function
- c_2 is the factor that results in an equipotential energy match of at least two of the participating atomic orbitals of each bond
- C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of a bond of the group
- C_{2o} is the factor that results in an equipotential energy match of at least two of the participating atomic orbitals of the transition state of the bond
- μ is the reduced mass

Condensed Matter Physics cont'd

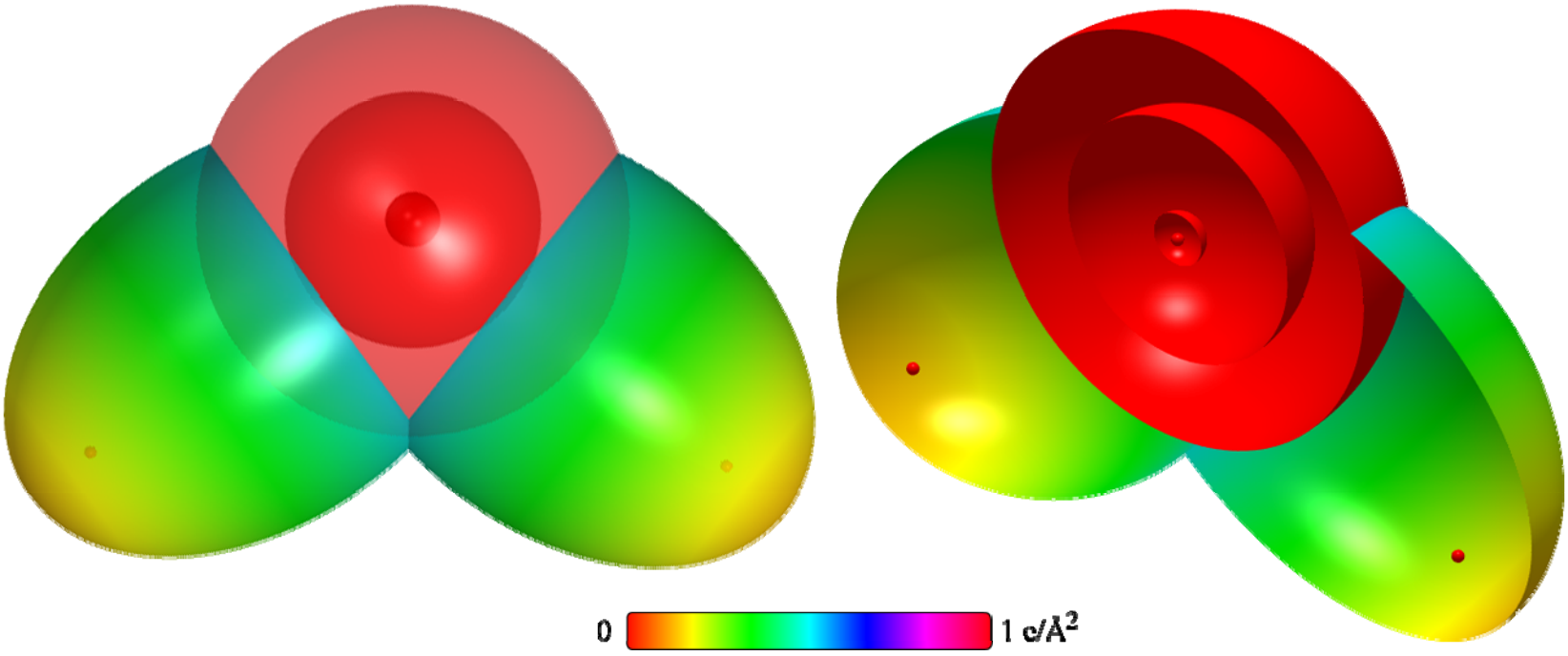
- Once the a, b, and c parameters of the unit cell are solved, then the unit cell can be proliferated to arbitrary scale to render the solid. The liquid is then, given as a linear combinations of units cells based on the solid cell whose structures and populations are based on statistical thermodynamical principles.

- A convenient method to calculate the lattice energy is to determine the electric field in the material having an electric polarization density, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

Geometrical Parameters and Energies of the Hydrogen Bond of H_2O

- H_2O MO comprises the linear combination of two O–H -bond MOs.
- Each O–H -bond MO comprises the superposition of an H_2-type ellipsoidal MO and the $O2p_z$ AO or the $O2p_y$ AO.

(A)-(B) Color scale, translucent views of the charge-density of the H_2O MO from the side-on and cross-section, respectively. For each O–H bond, the ellipsoidal surface of each H_2-type ellipsoidal MO transitions to the $O2p$ AO. The $O2p$ shell, the $O2s$ shell, the $O1s$ shell, and the nuclei (red, not to scale) are shown.



Geometrical Parameters and Energies of the Hydrogen Bond of H_2O cont'd

- The water molecule is small compared to the unit cell of ice; so, it will naturally assume a tetrahedral structure and hexagonal packing given the geometry of its electric dipoles with a partial positive on the *H*'s and partial negative on the *O*.

- The *O*–*H* bond has a bond moment μ of 1.51 D corresponding to a partial charge on each *H* of +0.323*e* and a component of partial charge on each *O* per bond moment of –0.323*e*.

- The geometrical parameters of ice are solved by first determining the separation distance of the electric monopoles based on the minimization of the Coulombic energy between the *H* and *O* of the hydrogen bond, limited by the formation of a nascent bond between these atoms that destabilizes the initial *O*–*H* bonds.

Geometrical Parameters and Energies of the Hydrogen Bond of H_2O cont'd

Using the parameters from the molecular solution of water, the equation for the balance of the Coulombic energy and the nascent $O–H$ bond energy of water is used to solve the semimajor axis of the nascent bond and thereafter the H -bond separation distance and the other geometrical and lattice parameters:

$$\frac{-4(0.323)^2 e^2}{4\pi\varepsilon_0\sqrt{\left(2\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}\right)^2+\left(5.2917706\,X\,10^{-11}\ m\right)^2}}$$

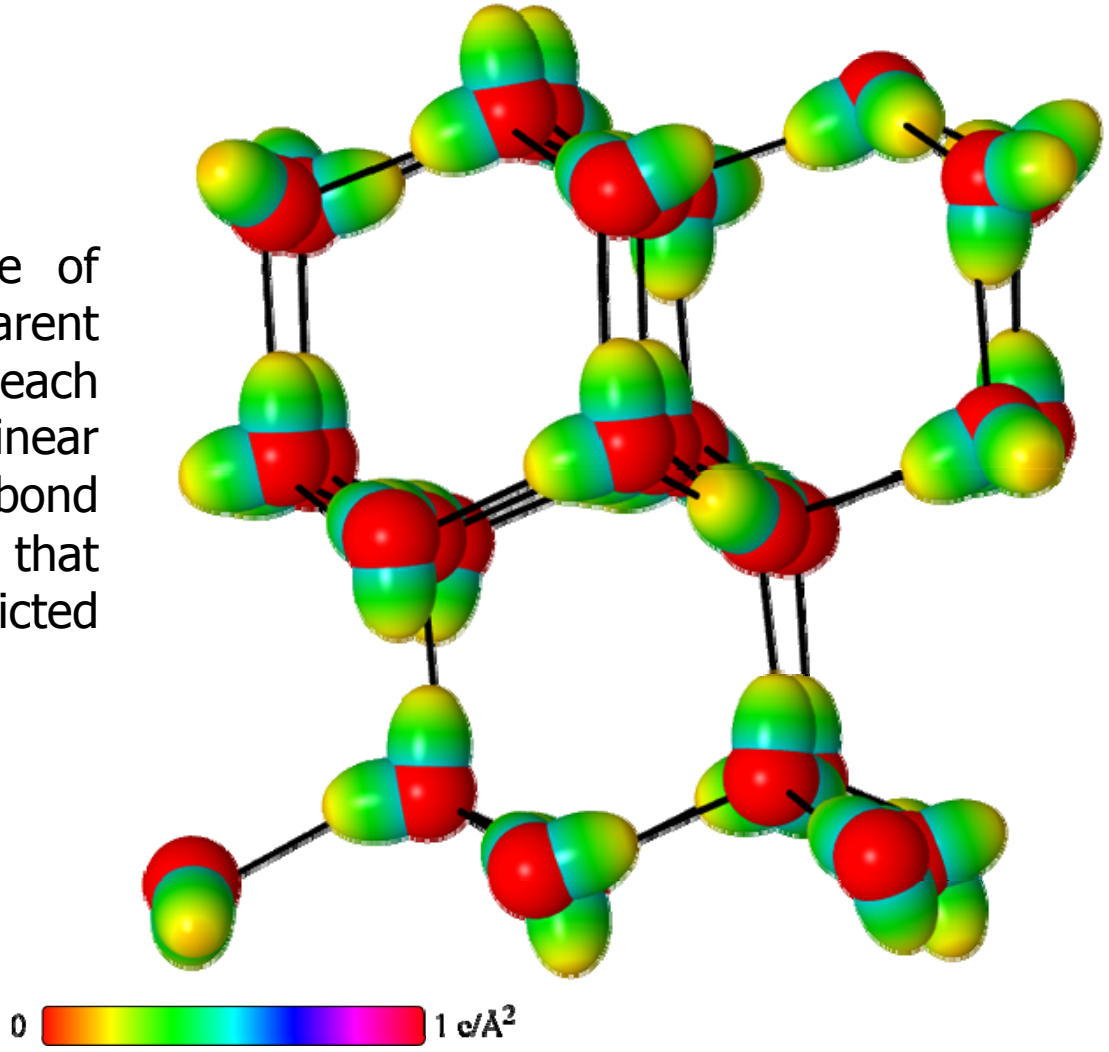
$$=\left\{\left(\frac{-e^2}{4\pi\varepsilon_0\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}}\right)\left(\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a_{O\cdots H}}\right)\ln\frac{a_{O\cdots H}+\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}}{a_{O\cdots H}-\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}}-1\right)\right\}$$

$$\left\{\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0\left(\sqrt{\left(a_{O\cdots H}\right)^2-\left(2\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}\right)^2}\right)^3}}{m_e}}{m_e c^2}}\right)\right.$$

$$\left.+2\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o\left(a_{O\cdots H}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{O\cdots H}+\sqrt{\frac{a_{O\cdots H}a_0}{2(0.75)}}\right)^3}}{\frac{16}{17}}}\right\}$$

Geometrical Parameters and Energies of the Hydrogen Bond of H_2O cont'd

Tetrahedral unit cell structure of Type I ice using the transparent color scale charge-density of each H_2O MO comprising the linear combination of two $O–H$ -bond MOs. Each dipole-dipole bond that is Coulombic in nature is depicted by connecting sticks.



Lattice Energy of Ice

A convenient method to calculate the lattice energy is to determine the electric field in ice having an electric polarization density corresponding to the aligned molecular water dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

The corresponding energy $U(H_2O)$ per water dipole due to the polarization electric field of the lattice of hexagonal dipoles is given by

$$U\left(H_2O\right)=2\mu_{H_2O}\cdot\mathbf{E}\left(H_2O\right)=\frac{-2\left(\mu_{H_2O}\right)^2\frac{\rho_{ice}}{MW}N_A}{3\varepsilon_0}$$

Lattice Energy of Ice Cont'd

The calculated and experimental geometrical and energy parameters of the H bond of water of Type I ice.

Parameter	Calculated	Experimental
H Bond Length $2c'_{O\cdots H}$	1.78219 Å	1.78 Å
Nearest Neighbor Separation Distance $2c'_{O\cdots HO}$	2.75377 A	2.75 Å
H_2O Lattice Parameter a_l	4.49768 A	4.49 Å 4.5212 Å
H_2O Lattice Parameter c_l	7.34077 Å	7.31 Å 7.3666 Å
Energy of Vaporization of Water at 0 °C	46.934 kJ/mole	45.054 kJ/mole

Lattice Energy of Ice Cont'd

- Using statistical mechanical models such as Boltzmann statistics to populate an increasing number of variants of the ice unit cell of increasing entropy while matching the internal energy at a given temperature, the structure of each phase of water is determined predominantly by the number of H bonds on average per water molecule.

- Based on the 10% energy change in the heat of vaporization in going from ice at 0°C to water at 100°C, the average number of H bonds per water molecule in boiling water is 3.6.

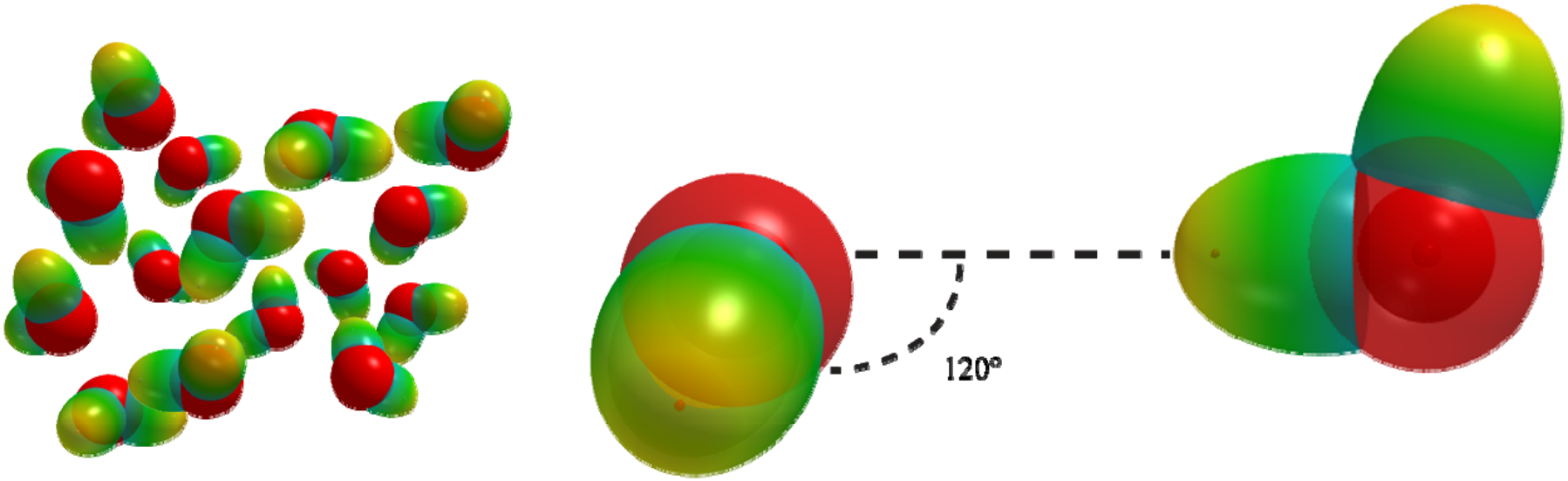
Steam

For the determination of the H-bond distance, the energy parameters, partial charge, and reduced mass are the same as those of the water molecules of ice except that the negative of the $E_{vapor,100°C} = 0.42137eV \ (40.657 \ kJ/mole)$ is equated to the nascent covalent bond energy corresponding to the limit of water vapor forming the condensed state.

The calculated and experimental geometrical parameters of the H bond of steam.

Parameter	Calculated	Experimental
H Bond Length $2c'_{O\cdots H}$	2.04501 Å	2.02 Å 2.05 Å
Nearest Neighbor Separation Distance $2c'_{O\cdots HO}$	3.01658 Å	3.02 Å

Structure of Steam



(left). Ensemble of gaseous water molecules undergoing elastic hard-sphere collisions.

(right). H-bonded water vapor molecules using the color scale charge-density of each H_2O MO comprising the linear combination of two $O-H$ -bond MOs.



Geometrical Parameters and Energies of the Hydrogen Bond of H_2O and NH_3

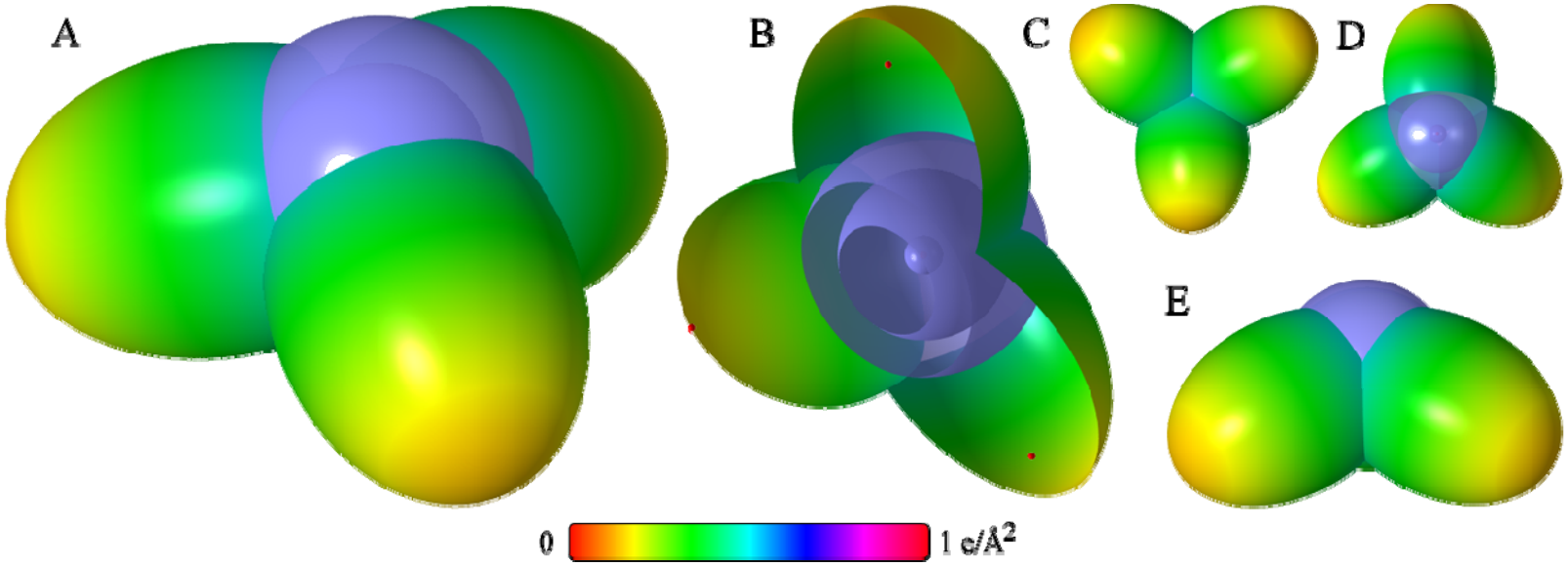
•The NH_3 MO comprises the linear combination of three $N-H$ -bonds.

•Each $N-H$ -bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $N2p_x$, $N2p_y$, or $N2p_z$ AO.

(A) Color scale, translucent view of the charge-density of the NH_3 MO shown obliquely from the top. For each $N-H$ bond, the ellipsoidal surface of each -type ellipsoidal MO transitions to a $N2p$ AO. The $N2p$ shell, the $N2s$ shell, the $N1s$ shell, and the nuclei (red, not to scale) are shown.

(B) Off-center cut-away view showing the complete inner most shell, and moving radially, the cross section of the $N2s$ shell, the $N2p$ shell, and the H_2-type ellipsoidal MO that transitions to a $N2p$ AO for each $N-H$ bond.

(C)-(E) Color scale, bottom, top, and side-on translucent views of the charge-density of the NH_3 MO, respectively.



Geometrical Parameters and Energies of the Hydrogen Bond of H_2O and NH_3 cont'd

- The $N-H$ bond of ammonia has a bond moment μ of 1.30 D corresponding to an N component of partial charge of $-0.262e$, and the $O-H$ bond has a bond moment μ of 1.51 D corresponding to an H partial charge of $+0.323e$.

- The geometrical parameters of the $H_3N\cdots H-OH$ H bond of the ammonia-water vapor molecular dimer are solved by first determining the separation distance of the electric monopoles based on the minimization of the Coulombic energy between the N and H of the hydrogen bond, limited by the formation of a nascent $N-H$ bond between these atoms that destabilizes the initial $N-H$ and $O-H$ bonds.

Geometrical Parameters and Energies of the Hydrogen Bond of H_2O and NH_3 cont'd

Using the parameters from the molecular solution of ammonia, the equation for the balance of the Coulombic energy and the nascent $N-H$ bond energy of the ammonia-water vapor molecular dimer is used to solve the semimajor axis of the nascent bond and thereafter the H -bond separation distance and the other geometrical parameters:

$$\frac{-3(0.262)(0.323)e^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)(0.93613)}}\right)}$$

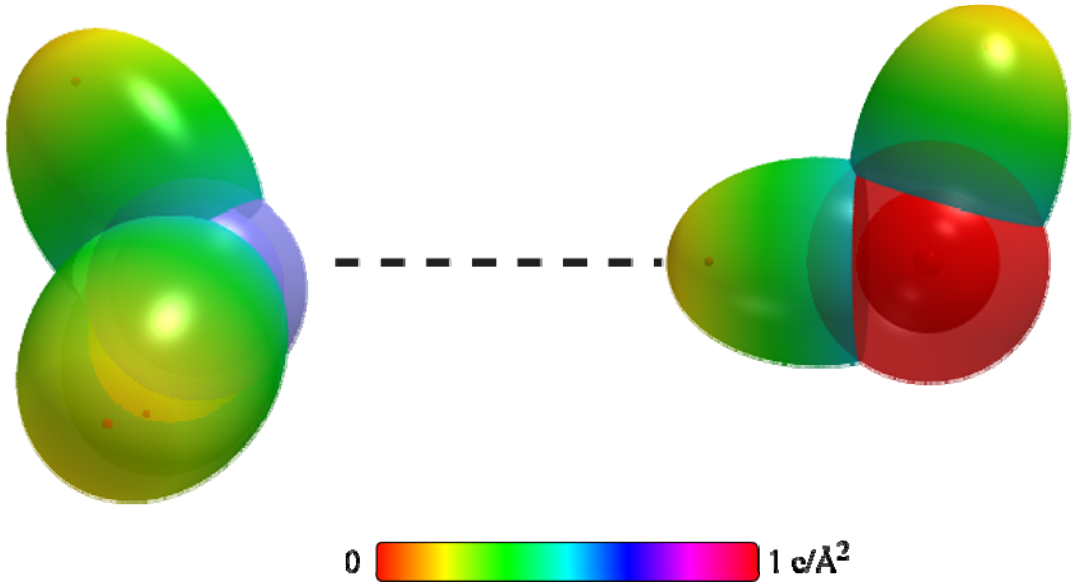
$$=\left\{\left(\frac{-3e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)(0.93613)}}}\left(\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a_{N\cdots H}}\right)\ln\frac{a_{N\cdots H}+\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)(0.93613)}}}{a_{N\cdots H}-\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)(0.93613)}}}-1\right)\right)\right.$$

$$\left.+3\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o\left(a_{N\cdots H}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{N\cdots H}+\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)(0.93613)}}\right)^3}}{\frac{14}{15}}}\right\}$$

$$\left\{\left(1+3\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0\left(\sqrt{\left(a_{N\cdots H}\right)^2-\left(2\sqrt{\frac{a_{N\cdots H}a_0}{2(0.75)}}\right)^2}\right)^3}}{m_e}}}{m_ec^2}}\right)\right.$$

Structure of the $H_3N\cdots H-OH$ H bond

The H-bonded ammonia-water vapor molecular dimer using the color scale charge-density of each NH_3 and H_2O MO comprising the linear combination of three $N-H$ and two $O-H$ -bond MOs, respectively.



Structure of the $H_3N\cdots H-OH$ H bond cont'd

The energy of forming the dimer in the gas phase is that of the alignment of the ammonia $H-N$ dipole in the electric field of the $H-O$ water dipole.

The $N\cdots H$ bond dissociation energy $E_D(N\cdots H)$ of the ammonia-water molecular dimer is

$$E_D\left(N\cdots H\right)=\mu_{H_3N}\cdot\frac{2\mu_{H-O,H_2O}}{4\pi\varepsilon_0\left(2c'_{N\cdots H}\right)^3}=\frac{\left(4.89196\ X\ 10^{-30}C\cdot m\right)\left(5.02385\ X\ 10^{-30}C\cdot m\right)}{4\pi\varepsilon_0\left(2.08186\ X\ 10^{-10}\ m\right)^2}=29.48\ kJ$$

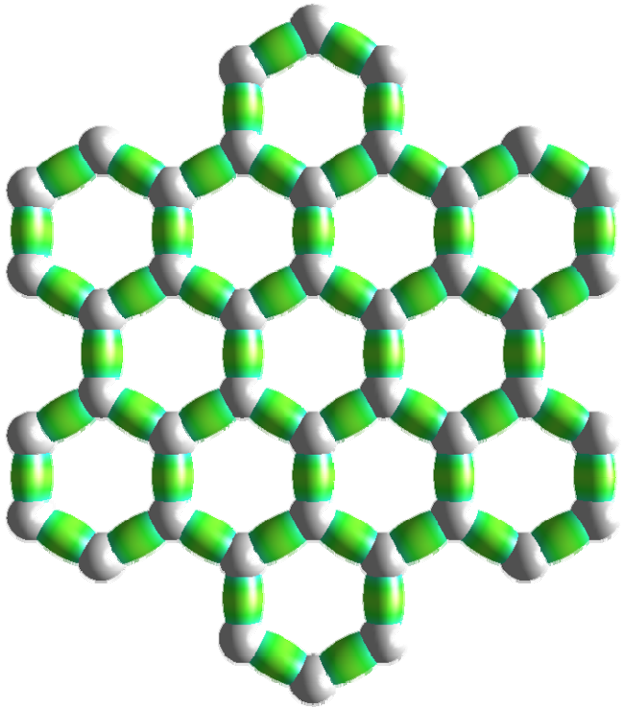
The calculated and experimental geometrical and energy parameters of H-bonded ammonia-water vapor molecular dimer.

Parameter	Calculated	Experimental
H Bond Length $2c'_{N\cdots H}$	2.08186 Å	2.02 Å
Nearest Neighbor Separation Distance $2c'_{N\cdots HO}$	3.05343 Å	2.99 Å
$N\cdots H$ Bond Dissociation Energy	29.48 kJ/mole	29 kJ/mole

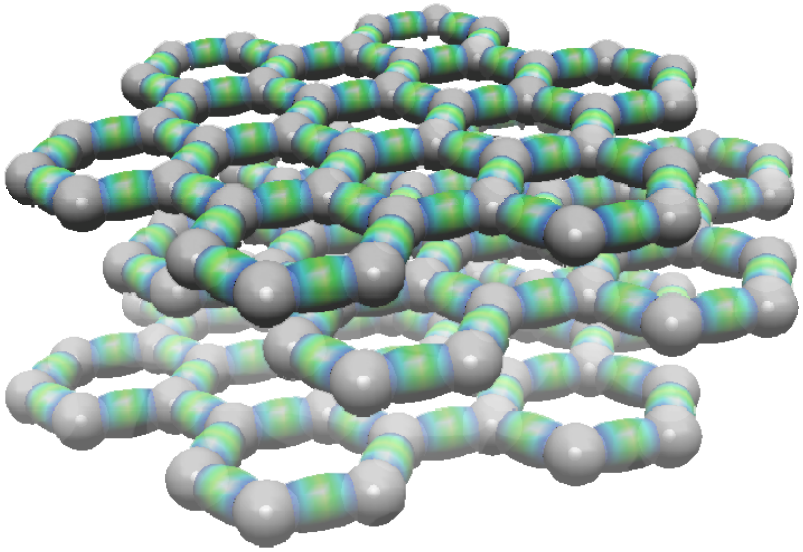
Geometrical Parameters Due to the Interplane van der Waals Cohesive Energy of Graphite

Graphite is an allotrope of carbon that comprises planar sheets of covalently bound carbon atoms arranged in hexagonal aromatic rings of a macromolecule of indefinite size.

A



B



A. Single plane of macromolecule of indefinite size.

B. Layers of graphitic planes with an interplane spacing of 3.5Å.

Geometrical Parameters Due to the Interplane van der Waals Cohesive Energy of Graphite cont'd

The van der Waals energy is due to mutually induced nonpermanent dipoles in near-neighbor bonds.

The $C \overset{8/3e}{=} C$ functional group of graphite comprises the aromatic bond with the exception that the electron-number per bond is $\frac{8}{3}$.

Albeit, the $C \overset{8/3e}{=} C$ functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 2.41270 D can be induced upon van der Waals bonding.

A minimum equal-energy is achieved throughout the graphite structure when each layer is displaced by $2c'_{C \overset{8/3e}{=} C}$, the bond length of $C \overset{8/3e}{=} C$, along an intra-planar C_2 axis relative to the next.

Then, a pair of dipoles exists for each dipole of a given plane with one dipole above and one below in neighboring planes such that all planes can be equivalently bound by van der Waals forces.

The van der Waals energy is the potential energy between interacting neighboring pairs of $C \overset{8/3e}{=} C$ induced dipoles.

Geometrical Parameters Due to the Interplane van der Waals Cohesive Energy of Graphite cont'd

The geometrical and energy parameters of graphite are calculated by equating the interplane van der Waals cohesive energy to the nascent bond energy:

$$\frac{-6\left(8.04790\,X\,10^{-30}\,C\cdot m\right)^2}{4\pi\varepsilon_0\left(\left(1.39140\,X\,10^{-10}\ m\right)^2+\left(2\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}\right)^2\right)^{1.5}}\cos\sin^{-1}\frac{2\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}}{\sqrt{\left(1.39140\,X\,10^{-10}\ m\right)^2+\left(2\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}\right)^2}}$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}}\left((0.85252)\left(2-\frac{1}{2}\frac{a_0}{a_{C\cdots C}}\right)\ln\frac{a+\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}}{a-\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}}-1\right)\right)\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)\frac{e^2}{4\pi\varepsilon_o\left(a_{C\cdots C}\right)^3}}{m_e}}}{m_e c^2}}\right)\right\}$$

$$+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{(0.85252)e^2}{8\pi\varepsilon_o\left(a_{C\cdots C}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{C\cdots C}+\sqrt{\frac{a_{C\cdots C}a_0}{2(0.5)}}\right)^3}}{6}}$$

Geometrical Parameters Due to the Interplane van der Waals Cohesive Energy of Graphite cont'd

The calculated and experimental geometrical parameters and interplane van der Waals cohesive energy of graphite.

Parameter	Calculated	Experimental
Graphite Interplane Distance $2c'_{C\cdots C}$	3.51134 Å	3.5 Å
van der Waals Energy per Carbon Atom	0.04968 eV	0.052 eV

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Liquid Helium

Noble gases such as helium are typically gaseous and comprised of non-interacting atoms having no electric or magnetic multipoles.

But, at very low temperatures these gases may be condensed with the formation of mutually induced, collision-mediated non-permanent van der Waals dipole interactions.

The dipoles are atomic rather than molecular, as in the case of graphite, and in both cases the limiting separation is based on the formation of a nascent bond to replace the dipole-dipole interaction.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Liquid Helium cont'd

The van der Waals bonding in the helium atom involves hybridizing the two $1s$ AO into $1s^2$ HO orbitals.

Albeit, the He functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 0.18049 D can be induced upon van der Waals bonding.

As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Liquid Helium cont'd

The geometrical and energy parameters of liquid helium are calculated by equating the interatomic van der Waals cohesive energy to the nascent bond energy:

$$\frac{-4\left(6.02040\ X\ 10^{-31} C\cdot m\right)^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{He\cdots He}a_0}{2(0.5)(0.93364)^{-1}}}\right)^3}$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{He\cdots He}a_0}{2(0.5)(0.93364)^{-1}}}}\left((0.93364)\left(2-\frac{1}{2}\frac{a_0}{a_{He\cdots He}}\right)\ln\frac{a+\sqrt{\frac{a_{He\cdots He}a_0}{2(0.5)(0.93364)^{-1}}}}{a-\sqrt{\frac{a_{He\cdots He}a_0}{2(0.5)(0.93364)^{-1}}}}-1\right)\right)\right.$$

$$\left.\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)(0.93364)^{-1}\frac{e^2}{4\pi\varepsilon_o\left(a_{He\cdots He}\right)^3}}{m_e}}{m_e c^2}}\right)\right.$$

$$\left.+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{(0.93364)e^2}{8\pi\varepsilon_o\left(a_{He\cdots He}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{He\cdots He}+\sqrt{\frac{a_{He\cdots He}a_0}{2(0.5)(0.93364)^{-1}}}\right)^3}}{2}}\right\}$$

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Liquid Helium cont'd

The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of liquid helium.

Parameter	Calculated	Experimental
Liquid Helium Interatomic Distance $2c'_{C\cdots C}$	3.70593 Å	3.72 Å (T=4.24 K) 3.70 (T<2.25K)
Roton Length Scale	3.70593 Å	3.7-4.0 Å
van der Waals Energy per Helium Atom (4.221 K)	0.000799 eV	0.000859 eV
Roton Energy	0.000799 eV	0.00075 eV

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Liquid Helium cont'd

The van der Waals energy and bond length matches the energy and length scale of the "roton," a characteristic quantized scattering element observed in liquid helium.

Liquid helium also possesses an interposed Bose-Einstein condensate (BEC) phase wherein the atomic translations are synchronous.

Since helium has only two electrons in an outer s-shell having a small diameter, the dipole moment is too very weak to form transverse dipoles associated with packing.

Specifically, with the angular dependence of packed dipoles interactions, the van der Waals energy between neighboring dipoles becomes less than the vibrational energy in the transition state.

Only linear chains and rings form and these structural elements give rise to quantized vortices and with the BEC phase, superfluidity.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Neon

In isolation or at sufficient separation, there is no energy between neon atoms.

However, reversible mutual van der Waals dipoles may be induced when the atoms are in close proximity such that neon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close face-centered cubic packing.

The van der Waals bonding in the neon atom involves hybridizing the three $2p$ AOs into $2p^3$ HO orbitals containing six electrons.

Albeit, the *Ne* functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 0.32544 D can be induced upon van der Waals bonding.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Neon cont'd

The geometrical and energy parameters of solid neon are calculated by equating the interatomic 12 nearest-neighbor van der Waals dipole energy to the nascent bond energy:

$$\frac{-24\left(1.08554\,X\,10^{-30}\,C\cdot m\right)^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{Ne\cdots Ne}a_0}{2(0.5)(0.89279)^{-1}}}\right)^3}\cos\left(\frac{\pi}{4}\right)$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{Ne\cdots Ne}a_0}{2(0.5)(0.89279)^{-1}}}}\left((0.89279)\left(2-\frac{1}{2}\frac{a_0}{a_{Ne\cdots Ne}}\right)\ln\frac{a+\sqrt{\frac{a_{Ne\cdots Ne}a_0}{2(0.5)(0.89279)^{-1}}}}{a-\sqrt{\frac{a_{Ne\cdots Ne}a_0}{2(0.5)(0.89279)^{-1}}}}-1\right)\right)\right.$$

$$\left.\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)(0.89279)^{-1}\frac{e^2}{4\pi\varepsilon_o\left(a_{Ne\cdots Ne}\right)^3}}{m_e}}{m_e c^2}}\right)\right.$$

$$\left.+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{(0.89279)e^2}{8\pi\varepsilon_o\left(a_{Ne\cdots Ne}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{Ne\cdots Ne}+\sqrt{\frac{a_{Ne\cdots Ne}a_0}{2(0.5)(0.89279)^{-1}}}\right)^3}}{10}}\right\}$$

Lattice Energy of Solid Neon

A convenient method to calculate the lattice energy is to determine the electric field in solid neon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

The corresponding energy $U(Ne)$ per neon dipole due to the polarization electric field of the lattice of face-centered cubic dipoles is given by

$$U(Ne) = \frac{-2(\mu_{Ne})^2 \frac{\rho_{solid\ Ne}}{MW} N_A}{3\varepsilon_0}$$

Lattice Energy of Solid Neon cont'd

The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid neon.

Parameter	Calculated	Experimental
Solid Neon Interatomic Distance $2c'_{C\cdots C}$	3.36683 Å	3.21 Å (T=24.48 K)
van der Waals Energy per Neon Atom	0.02368 eV	0.02125 eV

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Argon

In isolation or at sufficient separation, there is no energy between argon atoms.

However, reversible mutual van der Waals dipoles may be induced when the atoms are in close proximity such that argon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close face-centered cubic packing.

The van der Waals bonding in the argon atom involves hybridizing the three $3p$ AOs into $3p^3$ HO orbitals containing six electrons.

Albeit, the Ar functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 0.74366 D can be induced upon van der Waals bonding.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Argon cont'd

The geometrical and energy parameters of solid argon are calculated by equating the interatomic 12 nearest-neighbor van der Waals dipole energy to the nascent bond energy:

$$\frac{-24\left(2.48058\ X\ 10^{-30}\,C\cdot m\right)^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{Ar\ldots Ar}a_0}{2(0.5)(0.93660)^{-1}}}\right)^3}\cos\left(\frac{\pi}{4}\right)$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{Ar\ldots Ar}a_0}{2(0.5)(0.93660)^{-1}}}}\left((0.93660)\left(2-\frac{1}{2}\frac{a_0}{a_{Ar\ldots Ar}}\right)\ln\frac{a+\sqrt{\frac{a_{Ar\ldots Ar}a_0}{2(0.5)(0.93660)^{-1}}}}{a-\sqrt{\frac{a_{Ar\ldots Ar}a_0}{2(0.5)(0.93660)^{-1}}}}-1\right)\right)\right.$$

$$\left.\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)(0.93660)^{-1}\frac{e^2}{4\pi\varepsilon_o\left(a_{Ar\ldots Ar}\right)^3}}{m_e}}}{m_e c^2}}\right)\right\}$$

$$+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{(0.93660)e^2}{8\pi\varepsilon_o\left(a_{Ar\ldots Ar}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{Ar\ldots Ar}+\sqrt{\frac{a_{Ar\ldots Ar}a_0}{2(0.5)(0.93660)^{-1}}}\right)^3}}{20}}$$

Lattice Energy of Solid Argon

A convenient method to calculate the lattice energy is to determine the electric field in solid argon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

The corresponding energy $U(Ar)$ per argon dipole due to the polarization electric field of the lattice of face-centered cubic dipoles is given by

$$U\left(Ar\right) = \frac{-2\left(\mu_{Ar}\right)^2 \frac{\rho_{solid\ Ar}}{MW} N_A}{3\varepsilon_0}$$

Lattice Energy of Solid Argon cont'd

The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid argon.

Parameter	Calculated	Experimental
Solid Argon Interatomic Distance $2c'_{C\cdots C}$	3.62167 Å (T=0 K)	3.71 Å (T=4.2 K)
van der Waals Energy per Argon Atom	0.07977 eV (T=4.2 K)	0.08022 eV (T=0 K)

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Krypton

In isolation or at sufficient separation, there is no energy between krypton atoms.

However, reversible mutual van der Waals dipoles may be induced when the atoms are in close proximity such that krypton gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close face-centered cubic packing.

The van der Waals bonding in the krypton atom involves hybridizing the three $4p$ AOs into $4p^3$ HO orbitals containing six electrons.

Albeit, the Kr functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 1.01129 D can be induced upon van der Waals bonding.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Krypton cont'd

The geometrical and energy parameters of solid krypton are calculated by equating the interatomic 12 nearest-neighbor van der Waals dipole energy to the nascent bond energy:

$$\frac{-24\left(3.37329\ X\ 10^{-31} C\cdot m\right)^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{Kr\cdots Kr}a_0}{2(0.5)(0.92183)}}\right)^3}\cos\left(\frac{\pi}{4}\right)$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{Kr\cdots Kr}a_0}{2(0.5)(0.92183)}}}\left((0.92183)\left(2-\frac{1}{2}\frac{a_0}{a_{Kr\cdots Kr}}\right)\ln\frac{a+\sqrt{\frac{a_{Kr\cdots Kr}a_0}{2(0.5)(0.92183)}}}{a-\sqrt{\frac{a_{Kr\cdots Kr}a_0}{2(0.5)(0.92183)}}}-1\right)\right)\right.$$

$$\left.+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{(0.92183)e^2}{8\pi\varepsilon_o\left(a_{Kr\cdots Kr}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{Kr\cdots Kr}+\sqrt{\frac{a_{Kr\cdots Kr}a_0}{2(0.5)(0.92183)}}\right)^3}}{42}}\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)(0.92183)\frac{e^2}{4\pi\varepsilon_o\left(a_{Kr\cdots Kr}\right)^3}}{m_e}}{m_e c^2}}\right)\right\}$$

Lattice Energy of Solid Krypton

A convenient method to calculate the lattice energy is to determine the electric field in solid krypton having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

The corresponding energy $U(Kr)$ per krypton dipole due to the polarization electric field of the lattice of face-centered cubic dipoles is given by

$$U\left(Kr\right) = \frac{-2\left(\mu_{Kr}\right)^2 \frac{\rho_{solid\ Kr}}{MW} N_A}{3\varepsilon_0}$$

Lattice Energy of Solid Krypton cont'd

The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy (0 K) of solid krypton.

Parameter	Calculated	Experimental
Solid Krypton Interatomic Distance $2c'_{C\cdots C}$	4.08688 Å	3.992 Å
van der Waals Energy per Krypton Atom	0.11890 eV	0.11561 eV

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Xenon

In isolation or at sufficient separation, there is no energy between xenon atoms.

However, reversible mutual van der Waals dipoles may be induced when the atoms are in close proximity such that xenon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close face-centered cubic packing.

The van der Waals bonding in the xenon atom involves hybridizing the three $5p$ AOs into $5p^3$ HO orbitals containing six electrons.

Albeit, the Xe functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole of 1.41050 D can be induced upon van der Waals bonding.

Geometrical Parameters Due to the Interatomic van der Waals Cohesive Energy of Solid Xenon cont'd

The geometrical and energy parameters of solid xenon are calculated by equating the interatomic 12 nearest-neighbor van der Waals dipole energy to the nascent bond energy:

$$\frac{-24\left(4.70492\ X\ 10^{-31} C\cdot m\right)^2}{4\pi\varepsilon_0\left(2\sqrt{\frac{a_{Xe\cdots Xe}a_0}{2(0.5)(0.88682)}}\right)^3}\cos\left(\frac{\pi}{4}\right)$$

$$=\left\{\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{a_{Xe\cdots Xe}a_0}{2(0.5)(0.88682)}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a_{Xe\cdots Xe}}\right)\ln\frac{a+\sqrt{\frac{a_{Xe\cdots Xe}a_0}{2(0.5)(0.88682)}}}{a-\sqrt{\frac{a_{Xe\cdots Xe}a_0}{2(0.5)(0.88682)}}}-1\right)\right)\right.$$

$$\left.\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{(0.5)(0.88682)\frac{e^2}{4\pi\varepsilon_o\left(a_{Xe\cdots Xe}\right)^3}}{m_e}}{m_e c^2}}\right)\right.$$

$$\left.+\left(\frac{1}{2}\right)\hbar\sqrt{\frac{\frac{e^2}{8\pi\varepsilon_o\left(a_{Xe\cdots Xe}\right)^3}-\frac{e^2}{8\pi\varepsilon_o\left(a_{Xe\cdots Xe}+\sqrt{\frac{a_{Xe\cdots Xe}a_0}{2(0.5)(0.88682)}}\right)^3}}{65}}\right\}$$

Lattice Energy of Solid Xenon

A convenient method to calculate the lattice energy is to determine the electric field in solid xenon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation.

The corresponding energy $U(Xe)$ per xenon dipole due to the polarization electric field of the lattice of face-centered cubic dipoles is given by

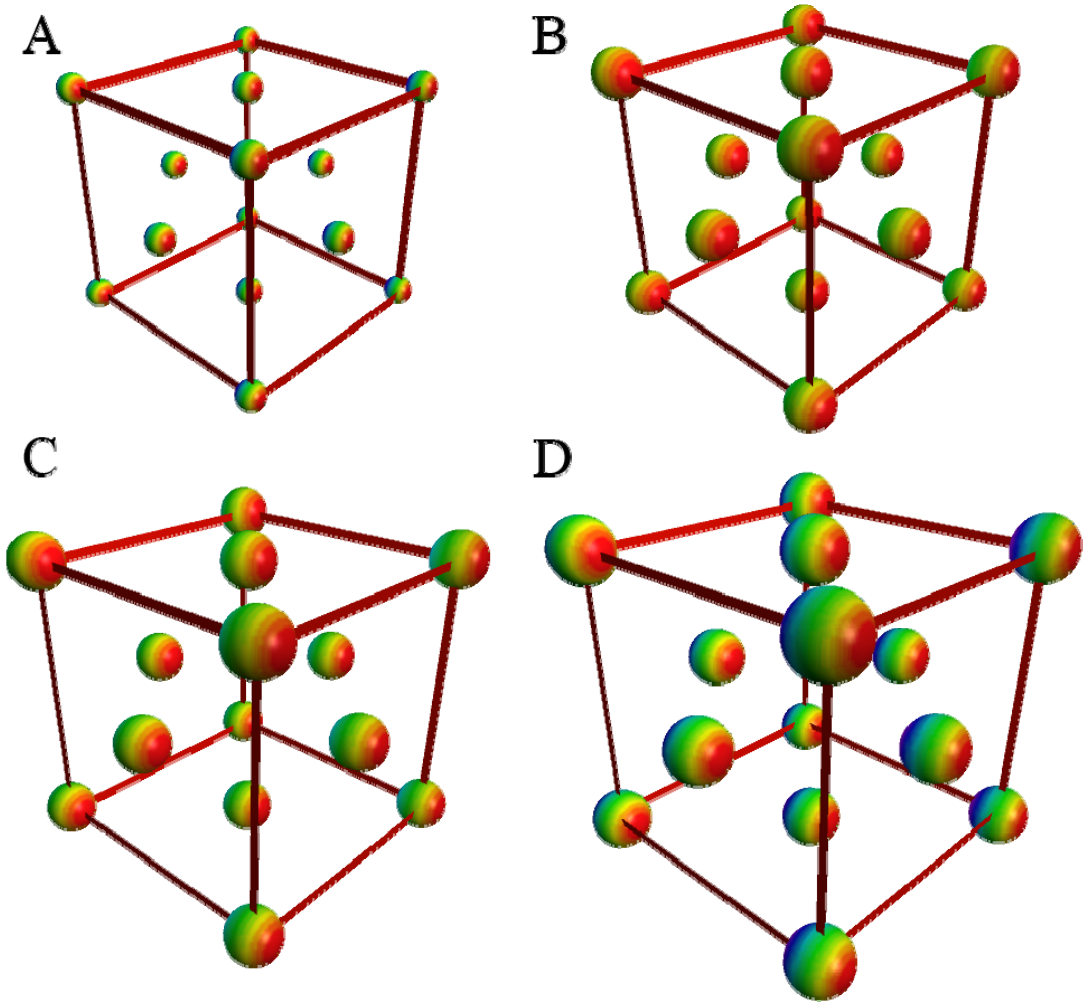
$$U\left(Xe\right) = \frac{-2\left(\mu_{Xe}\right)^2 \frac{\rho_{solid\ Xe}}{MW} N_A}{3\varepsilon_0}$$

Lattice Energy of Solid Xenon cont'd

The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid xenon.

Parameter	Calculated	Experimental
Solid Xenon Interatomic Distance $2c'_{C\cdots C}$	4.4884 Å (T=0 K)	4.492 Å (T=161.35K)
van der Waals Energy per Xenon Atom (0 K)	0.18037 eV	0.16608 eV

The charge densities of the van der Waals dipoles and face-centered cubic crystal structures of noble gas condensates, all to the same scale. (A) The charge density and crystal structure of neon. (B) The charge density and crystal structure of argon. (C) The charge density and crystal structure of krypton. (D) The charge density and crystal structure of xenon.



Reaction Kinetics and Thermodynamics

Reaction kinetics and thermodynamics are modeled using the classical solutions of reacting species, complexes, transition states, and products.

For the gas-phase reaction of two species A and B comprising the reactants that form one or more products C_n where n is an integer:

$$A + B \rightleftarrows C_1 + \cdots + C_n$$

the concentrations (denoted $[A]$, $[B]$,…) as a function of time can be fitted to a second-order rate law arising from collisional probabilities:

$$-\frac{d[A]}{dt} = k[A][B] - k' \prod_{i=1}^{n} [C_i]$$

where k and k' are the forward and reverse rate constants.

The equilibrium constant K corresponding to the balance between the forward and reverse reactions is given by the quotient of the forward and reverse rate constants:

$$K = \frac{k}{k'}$$

Reaction Kinetics and Thermodynamics

The relationship between the temperature-dependent equilibrium constant and the standard Gibbs free energy of reaction $\Delta G^{0}_{T}(T)$ at temperature T is

$$K = Q_K\left(T\right)e^{\frac{-\Delta G^{0}_{T}\left(T\right)}{RT}}$$

where R is the ideal gas constant,

$$Q_K\left(T\right) = \frac{\prod_{i=1}^{n}\left[C_i\right]}{\left[A\right]\left[B\right]}$$

is the reaction quotient at the standard state, and

$$\Delta G^{0}_{T}\left(T\right) = \Delta H^{0}_{T}\left(T\right) - T\Delta S^{0}_{T}$$

where $\Delta H^{0}_{T}\ (T)$ and ΔS^{0}_{T} are the standard-state enthalpy and entropy of reaction, respectively.

Rearranging gives the free energy change upon reaction in terms of the reaction quotient:

$$\Delta G = RTln\frac{Q_K}{K}$$

Transition State Theory

Transition state theory (TST) has been widely validated experimentally.

It entails the application classical trajectory calculations that allow the study of the dynamics at the microscopic level such as differential cross sections, total cross sections, and product energy distributions, as well as at the macroscopic level for the determination of thermal rate constants by solving the classical equations of motion with the formation of the transition state.

The data of the variation of the rate constant k with temperature of many reactions fit the Arrhenius equation given by

$$k = Ae^{\frac{-E_a}{RT}}$$

where E_a is the activation energy and A is a preexponential or frequency factor.

The Arrhenius equation confirms that typically two colliding molecules require a certain minimum kinetic energy of relative motion to sufficiently distort initial reactant bonds and concomitantly allow nascent bonds to form.

Transition State Theory cont'd

The cross over species from reactants to products called the transition state will proceed through the minimum energy complex involving the reactants.

Thus, the activation energy can be interpreted as the minimum energy that the reactants must have in order to form the transition state and transform to product molecules.

E_a can be calculated from the total energy of the transition state relative to that of the reactants and is achieved when the thermal energy of the reactants overcomes the energy deficit between the energy of the reactants and that of the transition state.

The preexponential factor corresponds to the collision frequency and energy of collisions upon which the formation of the transition state is dependent and is obtained by dynamical classical equations of motion involving species trajectories having typically a Maxwell-Boltzmann distribution.

S_N2 Reaction of Cl^- with CH_3Cl

The S_N2 (bimolecular nucleophilic substitution) gas-phase reaction of Cl^- with chloromethane proceeds through a transition state:

$$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$$

that obeys the Arrhenius equation

$$k(T) = \frac{k_B T}{h} \frac{Q^{\ddagger}}{\Phi^R} e^{\frac{-\Delta E^{\ddagger}}{k_B T}}$$

where k_B is the Boltzmann constant, h is Planck's constant, $\Delta E^{\ddagger}$ is the activation energy of the transition state $\ddagger$, T is the temperature, Φ^R is the reaction partition per unit volume, and $Q^{\ddagger}$ is the coordinate independent transition-state partition function.

S_N2 Reaction of Cl^- with CH_3Cl cont'd

The preexponential factor $\frac{k_B T}{h}\frac{Q^{\ddagger}}{\Phi^R}$ is calculated classically and shown to be in agreement with the experimental rate constant.

Then, only the transition state need be calculated, and its geometry and energy compared to observations to confirm that classical physics is predictive of reaction kinetics.

The activation energy is calculated by determining the energy at the point that the nascent bond with the chloride ion is the same as that of the leaving chlorine wherein the negative charge is equally distributed on the chlorines.

Transition State

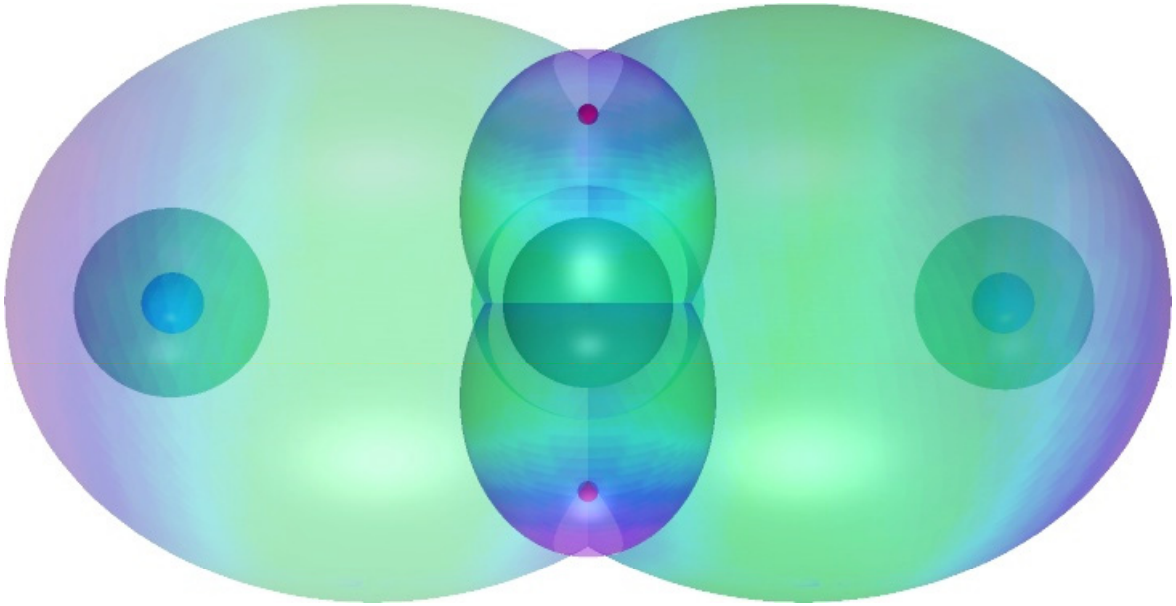
The reaction proceeds by back-side attack of Cl^- on CH_3Cl.

Based on symmetry, the reaction pathway passes through a D_{3h} configuration having $Cl^{\delta-} - C - Cl^{\delta-}$ on the C_3 axis.

The hydrogen atoms are in the σ_h plane with the bond distances the same as those of the alkyl CH_3 functional group, since this group is not involved in the substitution reaction.

The transition-state group $Cl^{\delta-} - C - Cl^{\delta-}$ is solved as a three-centered-bond functional group that comprises a linear combination of Cl^- and the $C - Cl$ group of chloromethane.

Transition State cont'd



Color scale, translucent view of the chloride-ion-chloromethane transition state comprising the $Cl^{\delta-} - C - Cl^{\delta-}$ functional group (hydrogen nuclei red, not to scale). As a symmetrical three-centered bond, the central bonding species are two *Cl* bound to a central CH_3^+ per $Cl^{\delta-} - C$ MO with a continuous current onto the $C - H$ MO at the intersection of each $Cl^{\delta-} - C$ MO with the CH_3^+ group. Due to the four electrons and the valence of the chlorines, the latter possess a partial negative charge of $-0.5e$ distributed on each $Cl^{\delta-} - C$ MO such that the far field is equivalent to that of the corresponding point charge at each Cl nucleus.

Transition State cont'd

The geometrical bond parameters of the $Cl^{\delta-} - C - Cl^{\delta-}$ and CH_3 functional groups of the chloride-ion-chloromethane transition state.

Parameter	$Cl^{\delta-} - C - Cl^{\delta-}$ Group	$C - H\ (CH_3)$ Group
$a\ (a_0)$	3.70862	1.64920
$c'\ (a_0)$	2.13558	1.04856
Bond Length $2c'\ (\AA)$	2.26020	1.10974
Literature Bond Length $(\AA)$	2.3-2.4	1.06-1.07
$b, c\ (a_0)$	3.03202	1.27295
e	0.57584	0.63580

The calculated bond energy of the $C - Cl$ group of chloromethane is $E_D\ (Group)\ (eV) = 3.77116\ eV$ is compared to the bond energy of the $Cl^{\delta-} - C - Cl^{\delta-}$ functional group of the chloride-ion-chloromethane transition state of $E_D\ (Group)\ (eV) = 3.73930\ eV$.

Since the energies of the CH_3 function groups are unchanged, the chloride-ion-chloromethane transition state is $\Delta E = +0.03186\ eV (+0.73473\ kcal/mole)$ higher in energy than chloromethane.

Experimentally, the transition state is about $1 \pm 1\ kcal/mole$ higher.

Using this energy as the corresponding activation energy $\Delta E^{\ddagger}$ with the classically determined preexponential factor $\frac{k_B T}{h}\frac{Q^{\ddagger}}{\Phi^R}$ predicts the experimental reaction rate very well.

Negatively-Charged Molecular Ion Complex $\mathbb{C}$

In addition to the nature and energy of the transition state designated by $\ddagger$, experimental gas-phase rate constants indicate that the reaction of Cl^- with CH_3Cl passes through a bound state comprising the attachment of Cl^- to the positive dipole of CH_3Cl.

This negatively-charged molecular ion complex designated $\mathbb{C}$ exists as a more stable state in between the reactants and the transition state, and by equivalence of the chlorines, it also exists between the transition state and the products.

Experimentally $\mathbb{C}$ is 12.2 ± 2 $kcal/mole$ more stable than the isolated reactants and products, Cl^- and CH_3Cl.

Thus, an energy well corresponding to $\mathbb{C}$ occurs on either side of the energy barrier of the transition state $\ddagger$ that is about 1 ± 1 $kcal/mole$ above the reactants and products.

Negatively-Charged Molecular Ion Complex $\mathbb{C}$ cont'd

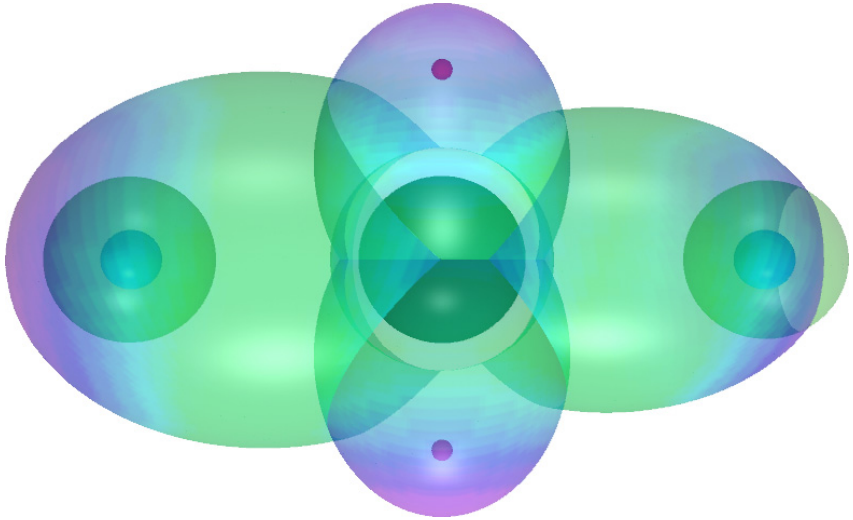
Thus, the combination of the depth of this well and the barrier height yields an intrinsic barrier to nucleophilic substitution of $13.2 \pm 2.2\ kcal/mole$.

The negatively-charged molecular ion complex $\mathbb{C}$ comprises the functional groups of CH_3Cl and a $Cl^- \cdot C^{\delta+}$ functional group wherein Cl^- is bound to the CH_3Cl moiety by an ion-dipole bond.

The bond energy and bond distance of the $Cl^- \cdot C^{\delta+}$ functional group are determined by the limiting energy and distance of the formation of a corresponding nascent $Cl^- - CH_3Cl$ covalent bond that destabilizes the $C - Cl$ bond of the CH_3Cl moiety by involving charge density of its electrons in the formation the nascent bond.

Subsequently, the higher energy $Cl^{\delta-} - C - Cl^{\delta-}$ functional group of the transition state is formed.

Negatively-charged Molecular Ion Complex $\mathbb{C}$ cont'd



Color scale, translucent view of the negatively-charged molecular ion complex $\mathbb{C}$ comprising the $Cl^{-}\cdot C^{\delta+}$ functional group (hydrogen nuclei red, not to scale). The bonding in the $\mathbb{C}$ complex comprises two paired electrons in the $Cl^{-}\cdot C^{\delta+}$ MO with 1/2 of the charge density from Cl^{-} and the other half from CH_3. The central bonding species are a Cl bound to a central CH_3^+ with a continuous current onto the $C-H$ MO at the intersection of the $Cl^{-}\cdot C^{\delta+}$ MO with the CH_3^+ group. Due to the two electrons and the valence of the chlorine, the latter possess a negative charge of $-e$ distributed on the $Cl^{-}\cdot C^{\delta+}$ MO such that the far field is equivalent to that of the corresponding point charge at the Cl nucleus. The bonding in the CH_3Cl moiety is equivalent to that of chloromethane except that the $C-H$ bonds are in a plane to accommodate the $Cl^{-}\cdot C^{\delta+}$ MO.

Negatively-Charged Molecular Ion Complex $\mathbb{C}$ cont'd

The geometrical bond parameters of the $Cl^{-} \cdot C^{\delta+}$, $C - Cl$, and CH_3 functional groups of the negatively-charged molecular ion complex $\mathbb{C}$.

Parameter	$Cl^{-} \cdot C^{\delta+}$ Group	$C-H$ (CH_3) Group	$C-Cl$ (i) Group
a (a_0)	2.66434	1.64920	2.32621
c' (a_0)	1.81011	1.04856	1.69136
Bond Length $2c'$ $(\mathring{A})$	1.91574	1.10974	1.79005
Literature Bond Length $(\mathring{A})$	>1.80 curve fit	1.06-1.07	1.785 (methyl chloride)
b,c (a_0)	1.95505	1.27295	1.59705
e	0.67938	0.63580	0.72709

The bond energies of the CH_3Cl moiety are unchanged to the limit of the formation of the $Cl^{-} \cdot C^{\delta+}$ functional group of the negatively-charged molecular ion complex $\mathbb{C}$.

Thus, the energy of stabilization of forming the ion-dipole complex is equivalent to the bond energy of the $Cl^{-} \cdot C^{\delta+}$ functional group.

Experimentally $\mathbb{C}$ is 12.2 ± 2 $kcal/mole$ more stable than the isolated reactants and products, Cl^{-} and CH_3Cl.

The calculated bond energy of the $Cl^{-} \cdot C^{\delta+}$ functional group of the negatively-charged molecular ion complex $\mathbb{C}$ of E_D $(Group) = 12.08900$ $(0.52422$ $eV)$ matches the experimental stabilization energy very well.

Reaction Mechanism

Animation of the reaction of chloride ion with chloromethane based on analytical solutions of the $\mathbb{C}$ complex and transition state.