**Properties**

**Introduction**

Most of the physical properties we are interested in are found by looking at the response of the electron density, wavefunction or energy to an "outside" influence. We say the potential and the electron density or energy have been perturbed. The "outside" influence can be something externally applied to the molecule by a person, like the magnetic field in an NMR experiment, or it may be because of something in the molecules immediate environment, like a charged ion or another molecule which has an instantaneous dipole.

Outside influences include

- electric field \((F)\)
- magnetic field \((B)\)
- light field
- relativistic effects (spin-orbit coupling)
- change in nuclear spin \((I)\)
- change in number of electrons \((n)\)
- change in nuclear positions \((R)\)

We measure the disturbance caused by these fields as derivatives, think of them as a parameter that measures the change in \(E\) for a given change in a field. For example the dipole moment of a molecule measures the change in \(E\) for a given change in the electric field \((F)\) around a molecule; \(\mu = \frac{dE}{dF}\). First derivatives are not the only property derivatives, second, third and even fourth derivatives of the energy give us useful properties. The most important ones are those which can also be measured experimentally. **Table 1** is a short list of some of the derivatives used to calculate physical properties \((F=\text{electric field}, B=\text{magnetic field}, I=\text{nuclear spin})\). While there are a large number of properties listed in **Table 1** we will be considering only the harmonic vibrational frequencies and the NMR shielding in detail.

<table>
<thead>
<tr>
<th>property</th>
<th>derivative (\frac{\partial E}{\partial F})</th>
<th>property</th>
<th>derivative (\frac{\partial E}{\partial B})</th>
</tr>
</thead>
<tbody>
<tr>
<td>dipole moment</td>
<td>(\mu)</td>
<td>magnetic dipole moment</td>
<td>(m)</td>
</tr>
<tr>
<td>polarizability (\alpha)</td>
<td>(\frac{\partial^2 E}{\partial F^2})</td>
<td>magnetizability (\xi)</td>
<td>(\frac{\partial^2 E}{\partial B^2})</td>
</tr>
<tr>
<td>harmonic vibrations</td>
<td>(\omega) (\frac{\partial^2 E}{\partial R^2})</td>
<td>spin-spin coupling (J)</td>
<td>(\frac{\partial^2 E}{\partial I^2})</td>
</tr>
<tr>
<td>IR intensities</td>
<td>(\frac{\partial^2 E}{\partial F \partial R})</td>
<td>NMR shielding (\sigma)</td>
<td>(\frac{\partial^2 E}{\partial B \partial I})</td>
</tr>
<tr>
<td>Raman intensities</td>
<td>(\frac{\partial^3 E}{\partial F^2 \partial R})</td>
<td>(ESR) hyperfine coupling constant (g)</td>
<td>(\frac{\partial E}{\partial I})</td>
</tr>
<tr>
<td>IR overtones</td>
<td>(\frac{\partial^3 E}{\partial F^2 \partial R^2})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1** Molecular properties are found by taking a derivatives of the energy. Most properties are very sensitive to electron correlation and so require a post HF method. Because many properties deal with the response of the electron density to...
external influences (ie fields), the static basis set must be flexible enough to describe the relocation of electron density. In general this requires a reasonable (DZ) basis set with polarization and diffuse functions.

**Frequency Analysis (IR and Raman spectra)**

The frequency analysis has an important role to play, not only does it provide the IR and Raman modes to compare with experiment, the derivative is also used in the analysis of critical points on the PES. Remember that we found that minima and maxima on the PES by testing the gradient or the first derivative of the energy. Then we discussed the curvature or the second derivative as the way of determining if the structure was a transition state (maximum energy) structure or minimum energy structure. If the second derivative (or curvature) is positive then it is a minimum and if the second derivative is negative it is a maximum. How then are these things linked, the frequency of a vibration and the curvature of a PES?

**Computing Vibrational Frequencies**

Let us go back to the potential energy surface which is described by the equation 

$$V(R) = V_{ne} + V_{ee} + V_{ae}. $$

We know roughly what $V(R)$ looks like, it is just a dissociation curve. $V(R)$ can be modelled, at least near the equilibrium distance by a quadratic function (a function of the form $y=mx^2$). You have seen this function before, it is called the harmonic oscillator (HO) function. For those of you who are a little more mathematical. We have expand $V(R)$ in a Taylor Series about the minimum $R_0$:

$$V(R) = V(R_0) + \left[ \frac{\partial V(R)}{\partial R} \right]_{R_0} (R - R_0) + \frac{1}{2} \left[ \frac{\partial^2 V(R)}{\partial R^2} \right]_{R_0} (R - R_0)^2 + O(R^n)$$

At the minimum the first derivative is zero, so \( \partial V(R)/\partial R=0 \), and we can define our axis system so that $V(R_0)=0$ at $R_0$, then we can truncate our expansion ignoring all the terms of $O(R^n)$ $n>2$, and this leaves us with only a single remaining term:

$$V(R) = \frac{1}{2} \frac{\partial^2 V(R)}{\partial R^2} R^2 = \frac{1}{2} k_R R^2 \text{ where } k_R = \frac{\partial^2 V(R)}{\partial R^2}$$

We have defined $k_R$ to be the second derivative, thus if $k_R$ is positive this is a minimum on the PES. $k_R$ is also called the force constant, for example a large force constant indicates a strong bond, and to stretch or contract a strong bond takes a large amount of energy. The solution of the HO problem also gives you the frequencies or vibrational modes of a molecule. Do you remember the relationship between $k_R$ and the wavenumber ($\omega$) (\( \mu \) is the reduced mass):

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k_R}{\mu}}$$

Thus the stronger the bond (\( k_R \)), the more energy must be expended to make the atoms vibrate, and the larger the wavenumber (\( \omega \)). We use IR and Raman spectroscopy to experimentally determine the vibrational frequencies or wavenumber (\( \omega \)) of a vibration, from this we can determine the force constant experimentally.
Computationally we find the force constant first (as the second derivative of the energy) and then compute the wavenumber.

However, the potential energy surface, as you know does not depend on a single coordinate, it is multi dimensional. Now that we have a multi-dimensional surface dependent on many coordinates, \( E(R_1, R_2, \cdots, R_N) \) how do we determine the stable geometries and transition states? Before we differentiated the energy with respect to one coordinate \( R \), now we have to differentiate with respect to each coordinate. At minima and transition states the force for every coordinate must be zero. If we write a list of the derivatives it would look something like the vector shown above.

We can also calculate a second derivative for each coordinate, however this is a little more complex than calculating the forces. The second derivative turns out to be a matrix, sometimes it is called the Hessian, and sometimes it is called the force constant matrix. In the Hessian matrix below the subscripts tell us which derivative has been taken.

\[
\begin{bmatrix}
  k_{11} & k_{12} & \cdots & k_{1(N-6)} \\
  k_{21} & k_{22} & \cdots & k_{2(N-6)} \\
  \vdots & \vdots & \ddots & \vdots \\
  k_{(N-6)1} & k_{(N-6)2} & \cdots & k_{(N-6)(N-6)}
\end{bmatrix}
\rightarrow
\begin{bmatrix}
  k'_{11} & 0 & \cdots & 0 \\
  0 & k'_{22} & \cdots & \vdots \\
  \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \cdots & k'_{(N-6)(N-6)}
\end{bmatrix}
\]

where:

\[
k_{11} = -\frac{\partial^2 E(R)}{\partial R_1 \partial R_1}
\]

\[
k_{12} = -\frac{\partial^2 E(R)}{\partial R_1 \partial R_2}
\]

and so on

In its basic form the Hessian matrix is not very useful, it is diagonalised to give us a new a new set of coordinates \( Q \) which are just linear combinations of the old coordinates and are called normal coordinates. Normal coordinates are just the vibrational modes, I’ve shown the normal coordinates or vibrational modes for \( \text{CO}_2 \) in Figure 3.

![Figure 3 Vibrational Modes =Q (for \( \text{CO}_2 \))](image)

Only at a minimum on the PES can the second derivative be equated to the vibrational force constant, as this is the only time they are all positive and real and observable. There is no physical relevance to a negative force constant or imaginary frequency. What about transition states? At transition states all the force constants for all of the coordinates except one must be zero. At the transition state we obtain a single negative force constant, or imaginary frequency (this is imaginary in the sense of complex numbers!), which has no physical relevance.

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relevance. The imaginary frequency that is isolated from a transition state structure is very useful, it gives us the coordinate that links the minima on either side of the transition state. In a rigorous examination of an energy surface, this coordinate will be followed to ensure that it leads to the "right" minima. This coordinate is called an intrinsic reaction coordinate (or IRC). If a particular structure is found that has two imaginary frequencies, then it is not a transition state.

Comparing Experimental and Computed Vibrational Frequencies

There is a problem in comparing computational and experimental frequencies. Frequencies are calculated using the Harmonic Oscillator approximation, while experimental frequencies include anharmonic effects. Actually we could calculate some of the anharmonic effects, they are just a higher derivatives, for example \( \frac{\partial^3 E}{\partial R^3} \). While frequency calculations can now be carried out routinely at a reasonable cost, third derivatives are too expensive and difficult to calculate routinely. Experimentally, the determination of harmonic frequencies is not practiced. Thus there is a gap between the quantity that is calculated and the quantity that is measured. There is a significant error \( \approx 10\% \) associated with equating calculated harmonic frequencies with experimental anharmonic frequencies, Table 2.

Computational and experimental spectra are routinely evaluated, and are commonly used to establish stable conformers and structures. Moreover the theoretical spectrum calculates all modes, including those that cannot be seen experimentally, this includes not only "forbidden" modes, but low energy fundamentals and modes which might otherwise be hidden due to overlapping matrix or solvent modes.

HF and DFT(LDA) methods can perform poorly. This is in part due to the poor (optimised) geometries determined by these methods. For example, the HF method underestimates M-L bonds, making them too weak and hence underestimates the force constants and associated frequencies. The HF method can reproduce scaled frequencies within 10-20cm\(^{-1}\), but only for simple organic molecules. Any system were correlation is important will not be well described. This includes systems with multiple bonds, transition metals, and open shell systems. The accuracy of the raw computed frequencies increases with method and basis set. For small molecules using a large basis set and a good method (for example: cc-pVQZ basis set at the CCSD(T) level) frequencies within 10cm\(^{-1}\) of the experimental values are reasonable. The remaining error is mostly due to anharmonic effects, and so there is really no point in going beyond MP2 unless you are going to calculate the anharmonic terms.

Due to this systematic difference between the calculated and experimentally determined quantity it has become popular to scale the computed frequencies. To obtain reliable frequencies correlation must be included, and large basis sets used, however, this error is also usually fairly uniform, and can be "included" in the empirical scaling factor. Table 3 shows scaling factors for a range of methods and the overall improvement in terms of deviation from the experimental values. The near unity scaling of the DFT(GGA) means that the "raw" data can be directly compared to

\[ \begin{array}{ccc}
\nu_1 & \nu_2 & \nu_3 \\
3756 & 3657 & 1595 \\
3943 & 3832 & 1649 \\
187 & 175 & 54 \\
\end{array} \]

\( \Delta \)

Table 2 Anharmonic and harmonic frequencies for water in cm\(^{-1}\), differences are \( \approx 3-5\% \)

\( ^{1} \)Data from "Introduction to Computational Chemistry" by Frank Jensen, John-Wiley & Sons, Chichester, 1999.
experiment (at a lower level of accuracy). This occurs because of a fortuitous cancellation of errors, not because the calculations are correct! So if you don't mind getting the right answer for the wrong reason, this is the method for you! The scaled DFT( Hybrid GGA) values are more accurate (in general) than the scaled QCISD values. Thus, for routine frequency analysis of medium to large molecules, DFT( Hybrid GGA) methods are the methods of choice.

There has been substantial work on the vibrational frequencies for small organic molecules. However the accuracy for a larger body of main group chemistry and transition metals, has not been investigated in any great depth. As we noted earlier it is not easy to accurately produce the geometry of TM complexes and this impacts on the calculated frequencies. For TM systems the HF method is inadequate, MP2 is usable for saturated non-3d TM systems, but DFT( Hybrid GGA) is by far the best option, both the B3LYP and BP86 functionals have been used to obtain reasonable predictions. Particular care has to be taken with TM-H bonds as they exhibit significant anharmonic effects and therefore reproducing accurate frequencies is difficult.

Frequency calculations are more useful than they might initially appear. The zero point energy of a molecule is determined, ie the energy tied up in the ν=0 vibrations. The calculation of isotopic frequencies is trivial once the primary calculation has been carried out, these are an invaluable diagnostic (isotopic frequency ratios) for the really hard core spectroscopists who are interested in nailing down the exact details in a spectrum. Once the vibrational modes are known thermodynamic properties (ΔG, ΔH, ΔS) can be also computed. The force constant for a bond stretch tells us how strong the bond is, how stiff the "electronic spring" between the atoms is, and this can be used to estimate the bond order. Bends also have a force constant, telling us how bendy, or how easy it is to distort the structure along the path of the vibration. It is all very well drawing the normal mode for a simple molecule, but when molecules get larger it becomes quite difficult to visualise how these motions work. In calculating the vibrational frequencies we also calculate Q, the form of the harmonic vibration. These can be visualised using a graphical interface, this can give you a deeper insight into the movement of the molecule than you would otherwise have had. This can be particularly important if you have several TS and only one of them joins your reactants with your products. Visual inspection can be very useful!

### NMR Chemical Shifts

Calculating NMR shielding constants is more complex and computationally demanding than calculating frequencies. The mathematics behind this is complex, so we will not discuss it. There are two key methods IGLO (Individual Guage for Localised Orbitals) and GIAO (Gauge Including Atomic Orbitals). The first chemically significant calculations were published in 1993 and used IGLO while most post 1996 implementations use GIAO. Reliable NMR chemical shift calculations

<table>
<thead>
<tr>
<th>Method</th>
<th>Scale Factor</th>
<th>Deviation (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.8953</td>
<td>50</td>
</tr>
<tr>
<td>DFT(LDA)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DFT(GGA)</td>
<td>0.9945</td>
<td>45</td>
</tr>
<tr>
<td>DFT(Hybrid GGA)</td>
<td>0.9614</td>
<td>34</td>
</tr>
<tr>
<td>MP2</td>
<td>0.9434</td>
<td>63</td>
</tr>
<tr>
<td>QCISD</td>
<td>0.9537</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 3 Variation in scaled frequencies (relative to experimental) for a range of methods using a small 6-31G(d) basis set based on a large data set of 122 small molecules representing 1066 fundamental modes.†


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have really only been produced since 1998. Chemical shieldings can be calculated for any nucleus, so not only $^1$H and $^{13}$C but also $^{15}$N, $^{17}$O, $^{29}$Si, $^{31}$P and heavier elements.

Experimentally chemical shifts are taken with respect to a reference molecule, TMS in the case of $^1$H and $^{13}$C NMR. When NMR parameters are calculated, it is the absolute shielding that is produced, so a second calculation on the reference molecule must always be performed to obtain the chemical shift as reported in experimental studies.

The interaction of a nuclear magnetic moment ($\mu$) with an external magnetic field (B) is modified by the shielding of the local electrons ($1-\sigma$). $\sigma$ is the nuclear shielding for nucleus A and is the second derivative of the total energy with respect to $\mu$ and B. $\sigma$ is a tensor (the mathematical name for a special type of matrix), and the rotational average, $\sigma$, is calculated as one third of the trace of the matrix, $\sigma_A$ is called the isotropic shielding constant. The $\delta$ referred to experimentally (in ppm) is just $\delta = \sigma_{\text{reference}} - \sigma$ for a particular nucleus.

$$E = -\mu_A \cdot (1-\sigma)B \quad \sigma_A = \frac{\delta^2 E}{\delta B \delta \mu_A} \bigg|_{B=0}$$

Without going into details, the calculation of NMR chemical shifts does not include some key contributions. To sidestep this issue is becoming common practice to calculate the NMR shielding for a molecule similar to the one under consideration and to use this as an intermediate reference. The experimental shifts of the intermediate reference molecule are then added to the computed chemical shifts, Figure 4. If the new reference has a similar electronic structure to the molecule under study, then deficiencies in describing the electronic structure will be common to both and thus systematic errors are eliminated by using an experimental (rather than the computed) chemical shift for the intermediate.

For example, to calculate the NMR chemical shifts of a series of compounds based around 3H-phenoxazin-3-one, Figure 5, the PBEPBE functional was used to calculate the absolute shifts of 1, 2, and 3 in CDCl$_3$ (PCM model) and benzene. The experimental shift of benzene (relative to TMS) was then added to the calculated shift $^{13}$C relative to the experimental $^{13}$C shift for benzene, the final number giving an estimate of the experimental shift of the compound relative to TMS. The results, averaged over all $^{13}$C atoms, are accurate to within 1.35ppm.

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NMR experiments are always carried out in a solvent. Introducing solvents into a computational investigation is difficult. However, one method is becoming more routine, it is based on treating the solvent as polarizable field. The equations for this are quite complex and beyond the scope of this course, however, think of a "polarizable field", as adding a term to the Hamiltonian which represents the electric field a solvent might produce around a molecule, Figure 6. There are no explicit solvent molecules. The solute is placed inside a cavity (formed from a set of spheres centered on the solute atoms or atomic groups). A particular functional group within a molecule might have a $\delta$- charge which will produce a corresponding localisation of charge on the cavity surface, the molecule will reorientate to take advantage of this energy lowering attraction. How responsive a particular solvent is depends on things like the solvent viscosity and charge density and is "summed up" into a single parameter, the dielectric constant ($\varepsilon$). For example cyclo-hexane, a non-polar solvent has $\varepsilon=2.023$ and water, a polar solvent has $\varepsilon=78.39$. You can think of the local build up of charge in the solvent as polarizing the quantum mechanical wavefunction. Because the solvent molecules are not treated explicitly continuum models are quite efficient. The two most popular implementations of this model are, the Polarized Continuum Model, PCM, and the Conductor-Like Screening Model, COSMO.

The chemical shielding depends on the electronic structure very close to the nuclei. However it has been found that chemical shifts are significantly influenced by the part of the valence orbitals that touches a core region. You can think of the small component of the valence orbital near the atomic core of the atom the orbital is centered on, and also the extreme tail of the valence orbital that lies close to the core of another nucleus (ie a bonded atoms core). Thus basis sets must ensure a good core description and a very good description in the orbital tails of the valence electrons. A suitable basis set for carrying out NMR calculations is triple zeta with polarization functions, thus a suitable Pople basis set would be 6-311+G(d,p). For more accurate results a single point energy calculation using, 6-311++G(2df,p) would be advisable. For cheaper but still reasonable results on organic systems, 6-311+G(d,p) energies on top of a 6-31G(d) geometry have been successful. Better basis sets constructed explicitly to obtain good NMR parameters are also available, one of these is called the IGLO-III basis set.

Near the cores of heavy elements electrons travel near the speed of light and relativistic effects are very large. NMR parameters are highly dependent on core electronic properties and thus in order to obtain accurate results relativistic effects must be recovered. Relativistic effects are very important for the chemical shifts of heavy elements, and lighter elements, when they are coordinated to a heavier metal. PPs cannot be used on the atom for which NMR parameters are to be computed. PP only recover relativistic mass effects, and not spin-orbit coupling effects, if a large amount of spin-orbit coupling is present, then a relativistic Hamiltonian is required.

Results from a recent study of $^{13}$C chemical shifts for small organic molecules have been reproduced in Table 4. It is clear that the HF and DFT(LDA) methods should not be used to determine NMR shifts. Somewhat surprisingly it was found that the DFT(Hybrid GGA) and DFT(GGA) both perform badly. The most well known DFT functionals were developed before magnetic field calculations were possible and P. Hunt, Feb 2008

![Figure 6 Continuum model for a solvent](continuum)
hence they were not "built" to produce accurate NMR parameters. More recently developed functionals can do significantly better, for example the GGA PBEPBE functional, which can perform better than the MP2 method. However, there is a problem in that there can be a significant variation in the accuracy of the GGA and Hybrid-GGA functionals, depending on the specific chemical system under study. We are left in the unpleasant position of having to say that sometimes they are quite good, but we can't say when those sometimes are!

Another problem in calculating experimentally relevant NMR chemical shifts, is that a number of conformers of a molecule may be present in solution. This means that all of the stable structures have to be identified, the chemical shifts for each compound computed and the average taken according to a Boltzmann distribution. Alternatively a molecular dynamics approach can be used to generate accessible structures, quantum chemical calculations are then performed on sample structures, and the "experimental" chemical shift is taken as the average of these computed values.

$^1$H chemical shifts are more difficult to predict than $^{13}$C chemical shifts, primarily because of the reduced spectral range and thus an error of even a tenth of a ppm is significant, while for $^{13}$C NMR an error of several ppm is sustainable. $^{17}$O chemical shifts are not well reproduced by DFT methods, and MP2 is recommended. It is important to note that any system with large amounts of non-dynamic correlation will generate not only bad, but completely useless results at all but the highest level of calculation. In Table 5 are some results for ozone, and MP2 is out by 3500ppm!

Spin-spin coupling constants can be calculated, however this technique is so new that there are few reports available in the literature. The current state of the art is therefore quite experimental and its accuracy unknown.

**Case 2: Si-Si Triple Bond**

**Motivation**

Unlike the C≡C triple bond which is very stable, the Si≡Si triple bond is not stable, and synthesising a structure with a Si≡Si triple bond has proven to be very difficult. The triply bonded structural isomers of Si compounds are less stable than isomers with a lower bond order, they are also highly reactive particularly toward dimerisation, Figure 7. In 1997 it was theoretically predicted that electronegative substituents could stabilise a C≡Si triple bond, subsequently the C≡Si triple bond was experimentally detected in 1999. Computational studies also confirmed the hypothesis that bulky substituents would restrict isomerisation and dimerisation, and hence they were not "built" to produce accurate NMR parameters. More recently developed functionals can do significantly better, for example the GGA PBEPBE functional, which can perform better than the MP2 method. However, there is a problem in that there can be a significant variation in the accuracy of the GGA and Hybrid-GGA functionals, depending on the specific chemical system under study. We are left in the unpleasant position of having to say that sometimes they are quite good, but we can't say when those sometimes are!

Table 4 Errors in NMR $^{13}$C chemical shifts, absolute and relative in ppm

<table>
<thead>
<tr>
<th>method</th>
<th>absolute (shielding)</th>
<th>relative (shifts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>8.5</td>
<td>8.1</td>
</tr>
<tr>
<td>DFT(LDA)</td>
<td>15.2</td>
<td>14.4</td>
</tr>
<tr>
<td>DFT(BLYP)</td>
<td>15.0</td>
<td>7.8</td>
</tr>
<tr>
<td>DFT(PBEPBE)</td>
<td>3.1</td>
<td>2.5</td>
</tr>
<tr>
<td>DFT(B3LYP)</td>
<td>13.0</td>
<td>7.9</td>
</tr>
<tr>
<td>MP2</td>
<td>5.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 5 NMR $^{17}$O chemical shifts (ppm) for ozone using aug-cc-pVQZ and better basis sets

<table>
<thead>
<tr>
<th>method</th>
<th>$O_{\text{terminal}}$</th>
<th>$O_{\text{central}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-2793</td>
<td>-2717</td>
</tr>
<tr>
<td>DFT(B3LYP)</td>
<td>-1673</td>
<td>-1115</td>
</tr>
<tr>
<td>DFT(PBEPBE)</td>
<td>-1453</td>
<td>-1040</td>
</tr>
<tr>
<td>MP2</td>
<td>+1055</td>
<td>+2675</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-1208</td>
<td>-754</td>
</tr>
<tr>
<td>experimental</td>
<td>-1254</td>
<td>-688</td>
</tr>
</tbody>
</table>

---

established that bulky groups stabilised disilynes relative to silyldienes. Crystal structures substantiating these studies for the heavier group fourteen elements were reported in 2000 and 2002. However the Si≡Si triple bond remained elusive.

Figure 7 (a) Possible isomers for HSi≡SiH, (b) Relative energy of stable structures

The first report claiming isolation of a disilyne, RSi≡SiR (R=SiMe(t-Bu$_3$Si)$_2$) appeared in 2004 and was based on a δ($^{29}$Si) NMR chemical shift of 91.5ppm because a crystal structure could not be obtained. This result was re-enforced by computational studies which showed that the RSi≡SiR isomer was 30 kcal/mol more stable than the R$_2$Si=Si isomer, and that the dimerisation reaction was endothermic. Later in 2004 the crystal structure of RSi≡SiR (R=Si-i-Pr[CH(SiMe$_3$)$_2$]) was reported, and the observed δ($^{29}$Si) NMR chemical shift for this compound was at 89.9ppm.

The work in this paper studies δ($^{29}$Si) NMR chemical shifts for a range of disilynes, comparing a range of methods, and confirms the assignment for RSi≡SiR (R=SiMe(t-Bu$_3$Si)$_2$) as that expected for s silicon atom in a Si≡Si triple bond.

Reference
Paper: M. Karni and Y. Apeloig, Organometallics, 2005, 24, 6319

Computational Details

- A variety of methods were employed:
  - DFT(Hybrid-GGA) primarily B3LYP but also BPW91, BP86 and HCTC407 correlation recovered with MP2 and CCSD(T)
  - Frequency analysis to confirm minima at the B3LYP/6-31G(d,p) level
  - NMR using GIAO
- A variety of basis sets were employed
  - base 1 = all 6-31G(d)
  - base 2 = all 6-31G(d,p)
  - base 3 = Si with 6-311G(d)
    H&C 6-31G(d)
  - base 4 = Si with 6-311G(3d)
    H&C 3-21G
  - base 5 = Si with 6-311G(3d)
    H&C 6-31G(d)
- Program packages include
  - Gaussian
  - Turbomole
  - AcesII

Geometries of the small model systems were optimized using the hybrid density functional method B3LYP22 with the 6-31G-(d,p)23 basis set. The large experimentally studied molecules RSi=SiR (R=SiMe(t-Bu$_3$Si)$_2$), Si-i-Pr[CH(SiMe$_3$)$_2$]2 and (E)-RCSi=SiCl (R=SiMe(t-Bu$_3$Si)$_2$) were optimized at B3LYP/6-31G(d), B3LYP/6-311G(d)[Si]:3-21G[C,H],24 and B3LYP/6-311G(d)[Si]:6-31G(d)[C,H].24 For the calculation of the NMR chemical shifts we used the GIAO ansatz25 with the B3LYP hybrid functional and with the BPW91,22d,26 BP86,22d,27 and HCTH40728 general gradient approximation (GGA) functionals and the MP229 and CCSD30 ab initio methods. These methods were accompanied by a variety of Pople’s basis sets23 augmented with d- and f-polarization functions as well as with diffuse functions on Si and C and p-polarization functions on H. Frequencies were calculated at B3LYP/6-31G(d,p) for the model systems in order to identify them as minima. The following basis set notations are used throughout the paper:24 base 1 = 6-31G(d); base 2 = 6-31G(d,p); base 3 = 6-311G(d)[Si]; 6-31G(d)[C,H]; base 4 = 6-311G(3d)[Si]:3-21G[C,H]; base 5 = 6-311G(3d)[Si]:6-31G(d)[C,H]. Geometry optimizations, frequency calculations, and NMR calculations by the DFT and MP2 methods were performed with the Gaussian 9831a and Gaussian 0331b series of programs. TURBOMOLE was used for the NMR calculations of RSi=SiR (R=SiMe(SiH$_3$)$_2$) at GIAO-MP2.32a The CCSD NMR values were calculated using ACESII.32b
The paper is split into two components, (I) evaluation of various computational methods and (II) analysis of $\delta^{(29)\text{Si}}$ NMR chemical shift for various triply bonded systems RSi≡SiR, including RSi≡SiR (R=SiMe($t$-Bu$_3$Si)$_2$). TMS is the reference compound and all calculations are based on same geometry; that computed at B3LYP/6-31G(d,p) level. Thus the only difference for each method is in the electronic structure. The evaluation was carried out to determine the best method for various requirements such as high accuracy, or computational tractability (i.e. for large molecules). In the tables below I have focused on the RSi≡SiR R=H molecules.

**Same methods using different basis sets:**
The authors have examined various basis sets, a subset of which are presented in Table 6. In their discussion the authors refer in the first instance to the absolute chemical shift $\sigma^{(29)\text{Si}}$ or "isotropic chemical shielding" and secondly to the relative chemical shift, $\delta^{(29)\text{Si}}$. For example on going from a double zeta 6-31G(d) to a triple zeta basis set 6-311G(d), the MP2 value for the absolute chemical shift changes by 61 ppm. Further changes effect the absolute chemical shift much less, adding more polarisation functions onto the heavy atoms, adding polarisation functions onto the H atoms, and adding diffuse functions. However the largest difference (which is between the 6-311G(d) basis set and the 6-311G(3d) basis set) is still reasonable ≈15 ppm. Of course changing the basis set effects the reference molecule as well, and thus differences between the relative chemical shifts, $\delta^{(29)\text{Si}}$ are much less. For example that between the double zeta 6-31G(d) to a triple zeta basis set 6-311G(d) at the MP2 level results in a change of only 4.3 ppm.

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\sigma^{(29)\text{Si}}$</th>
<th>$\delta^{(29)\text{Si}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(d)</td>
<td>458.3</td>
<td>-16.5</td>
</tr>
<tr>
<td>6-311G(d)</td>
<td>397.3</td>
<td>-20.8</td>
</tr>
<tr>
<td>6-311G(d,p)</td>
<td>402.3</td>
<td>-23.2</td>
</tr>
<tr>
<td>6-311G(2d)</td>
<td>389.9</td>
<td>-24.7</td>
</tr>
<tr>
<td>6-311+G(2df,p)</td>
<td>394.8</td>
<td>-27.7</td>
</tr>
<tr>
<td>6-311G(3d)</td>
<td>387.2</td>
<td>-26.0</td>
</tr>
</tbody>
</table>

**Table 6 MP2 level calculations**

**Different methods using the same basis set:**
Again in their discussion the authors refer in the first instance to the absolute chemical shift $\sigma^{(29)\text{Si}}$ and secondly to the relative chemical shift, $\delta^{(29)\text{Si}}$. From Table 7 it is clear that there is significant variation with respect to method, and that the B3LYP functional is not performing well, a newer functional called HCTH407 is doing much better, especially with the 6-311G(3d) basis set where the difference with respect to the CCSD $\delta^{(29)\text{Si}}$ values is only 1 ppm. The authors are following a typical procedure where experimental values are not avaible, and comparing calculated values of lower level methods with well trusted methods that include explicit electron correlation such as MP2 and CCSD. Note however that the basis sets possible with higher level methods are not as extensive, and so the best calculation using the CCSD method is restricted to a lower basis set, than the best calculation with the MP2 method, which uses a very large basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>6-311+G (2df,p)</th>
<th>6-311G (3d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-2.9</td>
<td>-</td>
</tr>
<tr>
<td>B3LYP</td>
<td>+0.4</td>
<td>-5.4</td>
</tr>
<tr>
<td>BPW91 &amp; BP86</td>
<td>-1.4</td>
<td>-8.7</td>
</tr>
<tr>
<td>HCTH407</td>
<td>-14.8</td>
<td>-20.2</td>
</tr>
<tr>
<td>MP2</td>
<td>-29.1</td>
<td>-26.0</td>
</tr>
<tr>
<td>CCSD</td>
<td>-</td>
<td>-19.1</td>
</tr>
</tbody>
</table>

**Table 7 Comparing methods.**

Further Testing:
The authors go on to further test the best DFT method (HCTH407 functional with the 6-311G(3d) basis set) against more molecules, some which have been experimentally characterised, Table 8. They show that the experimental and computational results match up well.
are in excellent agreement. In contrast (and not shown here) the B3LYP functional performs quite poorly shifting the $\delta^{29}\text{Si}$ downfield $\approx 30$ ppm.

**Analysis**

Calculations are not limited by our ability to crystallise or experimentally characterise a particular compound, and this allows us to examine series of much simpler molecules in order to try and understand the effects of specific changes on the electronic structure. Moreover calculations can be used to vary one parameter while leaving all others unchanged to gain insight into the electronic structure. For example, there is an expectation that more electronegative substituents on carbon will cause shifts to lower field (higher $\delta$ value), and more electropositive substituents will cause a shift to higher field (lower $\delta$ value). This simplistic hypothesis can be easily examined for $\text{RSi} \equiv \text{SiR}$ by analysing $\delta^{29}\text{Si}$ for $R=\text{H}$ ($\approx -23$ ppm), $\text{CH}_3$ ($\approx 15$ ppm) and $\text{SiH}_3$ ($\approx 69$ ppm).

Thus, in contrast to the simplistic hypothesis, as the substituent becomes more electropositive the $\delta^{29}\text{Si}$ chemical shifts move to lower field. The same occurs for $\delta^{13}\text{C}$ shifts in $\text{RC} \equiv \text{CR}$ when $R=\text{SiH}_3$ ($\approx 113$ ppm) there is a lower field shift (cf $R=\text{CH}_3$ ($\approx 76$ ppm)).

The power of computational analysis is in being able to explain why a particular anomaly occurs. In this case the explanation relates to a paramagnetic contribution to the chemical shielding. Paramagnetic effects induce currents that cause a local enhancement of the magnetic field causing downfield shifts. Theoretically these can be related to an interaction (or coupling) between the occupied and virtual orbitals of a molecule. The molecular orbitals (MO) have to be close in energy before they can interact, and so the key orbitals are those in the HOMO-LUMO region of the molecule. When a lone pair, or double or triple bond exist in the molecule it is generally interactions (or excitations) from a $\sigma$-type MO to a $\pi^*$-type MO that are important. The authors find that the energy gap between the $\sigma$-$\pi^*$ MOs is much smaller in $\text{RSi} \equiv \text{SiR}$ when $R=\text{SiH}_3$ compared to $R=\text{H}$, and even that $\beta$-substituents can effect this energy gap.

It is also found that the the $\delta^{29}\text{Si}$ chemical shift is extremely sensitive to the trans-bent angle, **Figure 8**. Calculations were carried out slightly altering the trans-bent angle and then evaluating the response or change in the $\delta^{29}\text{Si}$ chemical shift. A strong correlation was found with the $\cos^2 \theta$ and $\delta^{29}\text{Si}$ of $\approx 0.99$, and this was related to the overlap of pAOs in the $\sigma$-MO of the molecule. In the linear structure there is maximum overlap of the pAOs however as the substituents bend the overlap decreases and the energy of this orbital rises, closing the energy gap with the unoccupied $\pi^*$-MOs. This then allows the now high energy $\sigma$-MO to interact more strongly with the $\pi^*$-MO inducing paramagnetic currents and shifting the $\delta^{29}\text{Si}$ chemical shift to lower field. A smaller trans-bent angle, for example, due to steric repulsion will cause the opposite effect, moving the $\delta^{29}\text{Si}$ chemical shift to higher field.

<table>
<thead>
<tr>
<th>RR’Si=SiR’</th>
<th>HCTH407</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R'=\text{SiH}_3$</td>
<td>$R=\text{SiH}_3$</td>
<td>119.4</td>
</tr>
<tr>
<td>$R'=\text{Si}-t\text{-Bu}$</td>
<td>$R=\text{Si}-t\text{-Bu}$</td>
<td>149.3</td>
</tr>
<tr>
<td>$R'=\text{SiMe}_2-t\text{-Bu}$</td>
<td>$R=\text{SiMe}_2-t\text{-Bu}$</td>
<td>81.6</td>
</tr>
<tr>
<td>$R'=\text{Mes}$</td>
<td>$R=\text{Mes}$</td>
<td>60.7</td>
</tr>
</tbody>
</table>

**Table 8** Calculated for optimised structure, NMR $\delta^{29}\text{Si}$ values determined using 6-311G (3d). Experimental results are solid state. *MP2 value. †solution phase.
The Si-Si bond distance and the torsion angle between the substituents also effect the \( \delta^{29}\text{Si} \) chemical shift, but to a smaller extent. I will not discuss these here, and leave it to you to read through the paper. The potential energy surface is very soft or flat with respect to the angle and bond changes, meaning that significant variation can occur for very little cost in energy. The responsiveness of the \( \delta^{29}\text{Si} \) chemical shift to the exact structure of the disilyne means that NMR can be a sensitive probe of the exact molecular geometry. However it also conversely means that the geometry must be predicted with great accuracy. Moreover, the large substituents that are used to facilitate crystalisation may induce a significant deformation of the geometry and thus alteration in the NMR chemical shifts. The use of large ligands, and the requirement of an accurate geometry, combined with the high computational level required to evaluate the \( \delta^{29}\text{Si} \) chemical shifts makes these systems very challenging to compute.

One aim of this paper was to predict the \( \delta^{29}\text{Si} \) chemical shift for the \( \text{RSi} \equiv \text{SiR} \) (\( R=\text{SiMe}(t-\text{Bu}_3\text{Si})_2 \)) molecule. The substituents on the Si groups will have a large number of possible isomers due to rotation about the Si-Si single bonds, Figure 9. Thus not only must the fully optimised geometry be correctly predicted, but the rotational transition states and other local minima be determined. These are discussed in detail in the paper, and I will not cover it here, however it is obvious that great deal of work has gone into determining these structures. Due to the low barriers for rotation, free rotation is likely in solution, and thus the final prediction for the \( \delta^{29}\text{Si} \) chemical shift must average over the computed \( \delta^{29}\text{Si} \) chemical shifts for all of these accessible minima. The final predicted \( \delta^{29}\text{Si} \) chemical shift for \( \text{RSi} \equiv \text{SiR} \) (\( R=\text{SiMe}(t-\text{Bu}_3\text{Si})_2 \)) is 88.0±5 ppm which is in excellent agreement with the experimental value of 91.5 ppm.

4. N. Takagi and S. Nagase, *European Journal of Inorganic Chemistry*, Theoretical study of an isolable compound with a short silicon-silicon triple bond, \( (tBu(3)Si(2))MeSiSi \) equivalent to $SiSiMe(SitBU(3))(2)$, (2002), 2775.