Chemical Education using Feelable Molecules

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Abstract

Two different approaches for the preparation of novel cost-effective molecular haptic applications (Figure 1) are described. The former utilises Perl scripting within a commercial molecular modelling package to generate static / animated H3D scene graphs for haptic CPK space-filling atomic perception. Within the second approach, key chemical concepts such as reactivity, acidity and periodicity can be investigated using prototype H3D user interfaces.

CR Categories: H.5.2 [Information Interfaces and Presentation (e.g., HCl)]; User Interfaces—Graphical User Interfaces, Haptic I/O; J.2 [Physical Sciences and Engineering]—Chemistry

Keywords: haptics, chemistry, education

1 Introduction

Chemists rely heavily upon visualization as a key to understanding and depicting chemical processes. The pioneering work of:

- Dalton (atoms)
- Loschmidt (2D diagrams)
- Hofmann (first physical model)
- van’t Hoff and le Bel ( stereochemistry)
- Bernal (plasticine model of liquid water)
- Corey, Pauling & Koltun (CPK space-filling models)
- Watson & (DNA)

have laid solid foundations, e.g. CPK colour scheme, for modern molecular graphics and 3D rapid prototyping technologies.

Representing molecules in terms of their equilibrium Lewis structures and reactions as a scheme allows perceptions of atom connectivity, bonding (e.g. ionic, covalent, dative, and multicentre banana bonds), bond order (e.g. single, aromatic, double, triple etc.), aromaticity (Kekulé vs resonant forms) and chirality. Aesthetic molecular models act as pedagogic tools for students. Dreiding & CPK physical models have been routinely used in the form of model kits to conceptualize 3D molecular structures for decades, e.g. DNA [Watson and Crick 1953] and myoglobin [Kendrew et al. 1958]. Plastic kits offer cheapness & portability and immediate tactile & visual messaging coupled with efficient user manipulation & interaction (e.g. conformational analysis, reactions & pseudorotation).

The same degree of interactivity & tactility from physical models can be obtained using rapid-prototyping to generate accurate models from experiment or virtual data. Although the cost of 3D printing has decreased, the technology still remains out of reach of most schools. Powder-based models allow incorporation of atom-specific CPK colours, but may be fragile; whilst hand-painted polymers are more robust. The models can be optically / magnetically tracked and spatially registered to generate an augmented reality (AR) application [Skawinski et al. 1995; Gillet et al. 2006].

Molecular graphics has enhanced the accessibility of molecular modelling techniques, and assisted in the analysis and interpretation of underlying theory, e.g. isosurface visualization via the Marching Cubes algorithm. Molecular graphics are commonly represented using ‘stick’ or ‘space-filling’ representations, analogous to physical models. Subtle variations include ‘tube’ and ‘balls & stick’. Inclusion of shading & lighting effects, coupled with an element-specific colour scheme improve visual perception. For large enzymes and proteins, the secondary structure is visualized by a ‘ribbon’ [Cai et al. 2006], where the backbone is depicted as cylinders (α-helices), flat arrows (β-sheets), or tubes (no regular structure).

2 Haptics

Haptics couples the sense of touch with a computer-generated scene and can be employed within high-end VR suites, where haptics enhances [Brooks 1977] 3D perception from single-/multiple-viewpoint active, passive or autostereoscopic technologies. Haptics cues can be divided into:

- force (kinesthetic) feedback - perceptions of resistive forces via robotic manipulators
• tactile feedback - perceptions of heat, pressure and texture, e.g. finger tip (135 sensors / cm², senses vibrations < 10 kHz, most sensitive at ≈ 230 Hz [Burdea and Coiffet 1994])

Recent computer gaming advancements has seen affordable haptics (Table 1) and stereographics (via economical but more powerful graphics cards and eyewear) which can be easily integrated into a classroom environment. The Novint Falcon utilised in this work, retails for ≈ £200 (a fraction of the related Force Dimension range).

<table>
<thead>
<tr>
<th>Device</th>
<th>Cost (£k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haption Virtuose</td>
<td>75</td>
</tr>
<tr>
<td>Sensable Phantom Premium</td>
<td>35-55</td>
</tr>
<tr>
<td>Force Dimension Delta</td>
<td>28-52</td>
</tr>
<tr>
<td>Force Dimension Omega</td>
<td>18-30</td>
</tr>
<tr>
<td>Immersion CyberTouch / CyberGrasp</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Sensable Phantom Desktop</td>
<td>10</td>
</tr>
<tr>
<td>Sensable Phantom Omni</td>
<td>2</td>
</tr>
<tr>
<td>Novint Falcon</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Inexpensive graphics with clear educational benefits [Chittaro and Serra 2004; Salzman et al. 1999; Saint-Eidukat et al. 1999; Mc-Clean et al. 2001; Riganelli et al. 2003] can be obtained from Web3D technologies e.g. VRML & X3D. Support for haptics has also been demonstrated by extending these environments, for example, as with the InstantReality (www.instantreality.org) and H3D (www.h3dapi.org) APIs. Our hypothesis is that these benefits, which include knowledge-building experiences and the ability to analyze phenomena from different points of view, will aid a student to efficiently learn and understand key chemical concepts.

Although a majority of educational haptic applications are primarily employed to train medical practitioners [John et al. 2001], the use of molecular haptics is becoming more prevalent. Improved perception of a virtual molecule can be obtained via cooperative de-convolution & interpretation of multiple cues - synaesthesia [Durie 2005]. The first documented haptic interface for scientific visualization was Project Groppe [Ouh-Yong et al. 1988] which allowed force field perception for molecular docking. Graphical rendering of a 3D molecular surface can be obtained using an atomic force microscope (AFM), where the probe tip feels the surface. Nanomanipulators (based upon AFMs) [Guthold et al. 2000] allow atoms to be strategically placed onto thin films allowing quantum dots & corrals to be studied. Furthermore, force-feedback haptics can also be merged with tactile responses from rapid prototyping models.

Nevertheless, beyond molecular docking applications, there appears to be scant focus upon the use of haptics to describe key chemical concepts based upon quantum phenomena such as reactivity, periodicity and acidity which are encountered within secondary and undergraduate education, but taught mathematically. Multiple sensory knowledge-building experiences via a combination of active and passive haptic exploration of these quantum phenomena to “touch the reality of the invisible” should enable students, particularly those with high practical aptitudes to postulate qualitative trends, and make successful predictions. In this paper we describe how we have addressed this gap through the use of a combination of Web3D technologies [Davies et al. 2005] and commodity haptics hardware (the inexpensive Novint Falcon). We aim to deliver cost-effective and portable chemistry educational tools based upon the open-source H3D API using two techniques:

• Perl scripting within a commerical molecular modelling suite
• hard-coding using web- / literature-based / computed data

In the former, ideal for teaching and research, Perl scripting [Davies et al. 2009] efficiently generates an ASCII H3D file for static / animated molecular systems allowing haptic perception of the CPK space-filling atomic model for post-visualization using a H3D viewer. Within the latter, key chemical concepts [Davies 2007] such as reactivity, acidity and periodicity can be investigated using prototype H3D user interfaces. It is envisioned that a symbiotic merging of haptics and quantum mechanical (QM) calculations would allow an undergraduate student to generate data, e.g. molecular geometry, force constants, orbital eigenvalues, atomic charges etc. and make qualitative predictions for unknown systems. Simpler lesson plans, utilising pre-defined data would be constructed for secondary education.

3 Materials Studio

Although commercial and academic molecular visualization / modelling software (e.g. NAMD, VMD, RasMol, PyMol etc.) are routinely employed within supercomputing centres and universities, they are either too financially (license fees) and / or too technologically demanding (understanding of quantum mechanics is required if it is not to be treated as a “black-box”) for use in schools, academies or colleges. Commercial software typically feature minimal support for haptic perception and immersive / non-immersive VR environments, although an increasing percentage (e.g. VMD, Chimera) are now capable of generating analgyph, passive (polarsed) or 3D-autostereoscopic OpenGL-based graphics.

Chemical information can be described by a varied array of widely differing file formats, ranging from ASCII files, e.g. SMILES, .xyz, .mol and .pdb etc. to XML-markups, e.g. CML (Chemical Markup Language). Although molecular file interconverters exists (e.g. Bel, OpenBabel), key data can sometimes be lost or may not be efficiently described. The expressiveness and extensibility of CML allows molecular data to be encoded and efficiently converted to X3D using an appropriate XML / XSLT style sheet [Polys 2003].

Materials Studio (www.accelrys.com/products/materials-studio) and its MaterialsScript API allows Perl scripting to control atomistic Forcite simulations, but focuses on a subset of the Visualizer functionality - the main chemistry model and its associated objects, e.g. creation of new atoms & bonds, geometry monitors, structural cleaning etc. Properties such as atomic coordinates, unit cell parameters, symmetry, bonding data etc. can be accessed from the Properties Explorer, allowing efficient creation of scene graphs within any graphical / haptic language, mirroring CML approaches.

3.1 Simple Static Molecules

The below Perl script generates an ASCII-based H3D file for post-visualization within any H3D / X3D viewer. The centre of mass is re-centered, whilst at present, a fixed (but editable) scaling is employed; to ensure that the model fits into the H3D viewer window. Atomic descriptors, e.g. colour, element and position can be probed via the Properties Explorer. The Perl script generates a simple CPK space-filling H3D scene graph, containing only centrosymmetric spherical primitives. A haptic SmoothSurface node within an object’s Appearance node allows the user to modify both the stiffness and velocity based damping of the surface of each sphere - default values were employed. An array within the Perl script identifies whether atoms have previously been defined. Node definition and instantiation using DEF and USE respectively allows for effective scene graphs where each instance possesses identical van der Waals radii and CPK colour, but different position. Other graphical representations based upon bonding descriptors and non-centrosymmetric primitives (requiring translation & rotation), e.g. stick, ball & stick and cylinders are being developed.
use strict; use MaterialsScript qw(:all); use Cwd;
my $Sdoc = $Documents("3KIN.xsd"); my $Satoms = $doc->DisplayRange->Atoms;
my $string = ""; my %def = (); my $count = 0;
my $Scentroid = $doc->CreateCentroid($Satoms);
Scentroid->CentroidXYZZ = Point([X => 0, Y => 0, Z => 0]); Scentroid->Delete;
sai("<Group>"); rt("<Transform scale = '0.05 0.05 0.05'>"); rt("<Group>");
foreach my $Satom (@$Satoms) {
    $count++; my ($red, $green, $blue) = atom
}
for (my $i = 0; $i < @$Satoms; $i++) {
    my $atom = "\""," atom
}
CreateCentroid($atoms);

The Perl script was tested for a series of proteins (Table 2, Figure 2) from the RCSB Protein Database (www.pdb.org) [Berman et al. 2000]. The motor protein 3KIN [Koziealski et al. 1997] is dimeric kinesin from Rattus Norvegicus; whilst 2A68 (566 metal ions) is t. Thermophilus RNA polymerase holoenzyme in complex with antibiotic rifabutin [Artsimovitch et al. 2005]. The largest system to date, a model of a bacteriophage phi-29 connector array [Guo et al. 2005] is stored as three files (1VRI, 1YWE & 1VRJ). Generation of the 1VRJ X3D file (12 MB from a 7 MB .pdb file) using a standard PC took no more than 5 minutes. Graphical & haptic rendering (NVIDIA Quadro FX4400G) is, however, too slow for real time.

<table>
<thead>
<tr>
<th>Table 2: Selected Macromolecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDB CODE</td>
</tr>
<tr>
<td>3KIN</td>
</tr>
<tr>
<td>2A68</td>
</tr>
<tr>
<td>1VRJ</td>
</tr>
<tr>
<td>1VRJ/1YWE</td>
</tr>
</tbody>
</table>

Figure 2: Selected H3D rendered macromolecules, 3KIN (left), 2A68 (middle), 1VRJ (right)

3.2 Periodic Systems

Figure 3: Selected NaCl unit cells: asymmetric (far-left), primitive (mid-left), conventional: 1 x 1 x 1 (mid-right), 2 x 2 x 2 (far-right)

Periodic cells e.g. polymers (1-D), surfaces (2-D) & crystals (3-D) can be infinitely extended. MaterialsScript API allows efficient interconversion between different representations for crystalline materials (Figure 3), without knowledge of space group symmetry. Inclusion of cell vectors is currently under development.

3.3 Molecular Dynamics (MD) and Vibrations

Addition of TimeSensor & Position Interpolator nodes with suitable routing allows keyframe animation (Figures 4-6). Since the trajectories start at frame 1, an initial frame (t = 0) is constructed from the parent system. The key Values attribute representing the change in atomic coordinates is obtained by looping through each frame per atom. For a $M$ frame trajectory with $N$ atoms, $M \times N$ frames must be loaded, leading to high I/O overheads:

```
my $Sdoc2 = $Documents("/test Disco Min/test Disco Dynamics/test.xsd");
my $Sdoc1 = $Documents("/test Disco Min/test.xsd");
my $Satoms = $doc->DisplayRange->Atoms; my $Straj = $doc2->Trajectory;

molecular rendering goes here
```

```
for(my $i=1;$i<=$Straj->NumFrames;$i++){
    $Straj->CurrentFrame = $i; $Skey = $key; $Skey=$Straj->NumFrames.;
    my $Stratoms = $doc2->DisplayRange->Atoms;
    $Svalue = $Svalue.(Stratoms->Item($i-1)->X: 
    "\".Stratoms->Item($i-1)->Y: 
    "\".Stratoms->Item($i-1)->Z: 
    "\";

    sai("<PositionInterpolator DEF="\"TS\" cycleInterval="\"10.0\" loop =\"true\"/>\"");
    $Skey = 0; foreach my $Satom (@$Satoms) { $i++; my $Skey = "0; "; my $Svalue = "";
    $Svalue = $Satoms->Item($i-1)->X: "$; $Satoms->Item($i-1)->Y: "$; $Satoms->Item($i-1)->Z: ";

    sai("<TimeSensor DEF="\"TS\" cycleInterval="\"10.0\" loop =\"true\"/>\"");
    $Skey = 0; foreach my $Satom (@$Satoms) { $i++; my $Skey = "0; "; my $Svalue = "";
    $Svalue = $Satoms->Item($i-1)->X: ""," $Satoms->Item($i-1)->Y: "; $Satoms->Item($i-1)->Z: ";

    sai("<ROUTE fromNode="\"TS\" fromFields="/fraction_changed/ 
    toNode="/Move", $i, "; toFields="/set_fraction"/>\"");
    sai("<ROUTE fromNode="/Move", $i, "; fromFields="/value_changed/ 
    toNode="/Atom", $i, "; toField="/set_translation"/>\"");
```

Figure 4: Diiodine reduction of cyclopropene: start (left), saddle / transition state (middle), end (right)

Figure 5: PVC MD simulation

Figure 6: C-H wagging libration (751 cm$^{-1}$) in benzene, C$_{6}$H$_{6}$
4 Periodicity

One of the foremost challenging subjects within the Chemistry curriculum is quantum mechanics and the subtle nuances it plays upon the chemical & physical properties. Prototype H3D interfaces are hereby presented which enable probing of key molecular properties such as reactivity, periodicity and acidity.

4.1 Reactivity

The bond energy, $E$, of a molecule is a measure of the strength of a chemical bond; the latter being related to the bond length and order (Tables 3 and 4). Although a Morse potential, $E = D_e(1-e^{-a(r-r_0)})^2$, correctly describes the bond energy, the harmonic oscillator, $E = k(r-r_0)^2$, where $k$ is the force constant (stiffness), and $r_0$ is the reference bond length is usually employed.

Table 3: Example Bond Energies: Force constants from [Anslyn and Dougherty 2006; Robinson and Lister 1963; Herzberg 1945; Lord and Andrews 1937]

<table>
<thead>
<tr>
<th>Bond</th>
<th>C-C</th>
<th>Ph</th>
<th>C≡C</th>
<th>C≡C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$ (kJ mol$^{-1}$)</td>
<td>348</td>
<td>519</td>
<td>614</td>
<td>839</td>
</tr>
<tr>
<td>$r_0$ (pm)</td>
<td>154</td>
<td>138</td>
<td>134</td>
<td>120</td>
</tr>
<tr>
<td>Bond Order</td>
<td>1.5</td>
<td>1.5</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$k$ (mdyn Å$^{-1}$)</td>
<td>4.5</td>
<td>7.6</td>
<td>9.7</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Table 5: Harmonic Springs in HX [Ladd 2008]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>H-F</th>
<th>H-Cl</th>
<th>H-Br</th>
<th>H-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (N m$^{-1}$)</td>
<td>966</td>
<td>516</td>
<td>412</td>
<td>314</td>
</tr>
<tr>
<td>$r_0$ (Å)</td>
<td>0.927</td>
<td>1.274</td>
<td>1.414</td>
<td>1.609</td>
</tr>
<tr>
<td>$D_e$ (kJ mol$^{-1}$)</td>
<td>565</td>
<td>431</td>
<td>366</td>
<td>299</td>
</tr>
</tbody>
</table>

A preliminary haptic model (Figure 7) for HX, X = F, Cl, Br, I was constructed using a single, white hydrogen (H) atom as a haptics probe. H3D API implements six different force effects:

- ForceField: applies a constant force to the scene
- MagneticEffect: models a spring
- PositionFunctionEffect: position-controlled forces
- TimeFunctionEffect: time-controlled forces
- SpringConstant: viscosity

Using a haptic SpringConstant node, a single harmonic spring (Table 5) was attached to each atom as shown in the below code sample. The SFVec3f position field of the springConstant node was vertically displaced so as to reproduce the equilibrium bond lengths. Identical SFFloat startDistance and escapeDistance fields indicating the distance from the centre of spring to where force starts / no longer acts upon the haptics device, were chosen ensuring that the force field begins to feel the spring whilst just outside the van der Waals radius of the halogen. Force constants applied using an SFFLoat springConstant field were scaled to generate an optimum working range of user haptic feedback (springConstant=100-500), resulting in force-feedback which is neither too weak nor too strong.

A class of 54 sophomores were invited to test the user interface. Without prior knowledge of the spring stiffesses, the majority (80%) correctly identified the strongest (H-F) and weakest (H-I) bonds. An improved interface is now capable of showing (or hiding) values for the respective force constants. Since the harmonic oscillator is encountered within the second undergraduate year, it is difficult to ascertain whether haptics significantly improves upon traditional student learning. Nevertheless, subsequent demonstrations for secondary school teachers and their students reveal substantial interest in this novel, practical way of teaching reactivity. The users translated the probe atom within the xy-plane prior to translation within the z-direction. Division of multidimensional tasks into a series of 1D/2D problems is common [Brooks 1977]. A mixture of active (the user controlled his / her own actions) and passive (the hand of the user and Falcon effector was guided by an observer) haptic exploration was employed, the latter ensuring complete devotion to object perception [Kennedy et al. 1992].

4.2 Ionization Potentials, IP and Electron Affinities, EA

The n$^{th}$ ionization potential, IP, is the energy required to strip it of the n$^{th}$ electron after the first n - 1 electrons have been removed, and is an excellent indicator of reactivity, measuring the reluctance of an atom / ion to surrender an electron. Similarly, the electron affinity, EA, is the energy released when removing an electron from a singly charged negative ion, i.e. X$^{-} \rightarrow X + e^{-}$, although the older convention, $X + e^{-} \rightarrow X^{-}$ (opposite sign) is also employed. Two prototype user interfaces (Figure 8) consisting of CPK atoms (attached harmonic spring), and a small haptic probe (electron) were constructed. In both applications, the user pulls the haptic probe (electron) from the atom - springConstant=100-500 representing the magnitude of the IP (Table 6 [Harrison 1984]) or EA (Table 7 [Huheey et al. 1997]). A logarithmic scaling was employed for the IPs (exponential growth for successive IPs), whereas a linear scaling was utilised for EAs. Although only demonstrated to a small group of secondary school teachers, we envisage that students via a constructed lesson plan, will feel trends within the 1$^{st}$ and 2$^{nd}$ IPs, enabling qualitative predictions for 3$^{rd}$, 4$^{th}$ & 5$^{th}$ IPs.

Figure 7: Reactivity Graphical User Interface

A mixture of active (the user controlled his / her own actions) and passive (the hand of the user and Falcon effector was guided by an observer) haptic exploration was employed, the latter ensuring complete devotion to object perception [Kennedy et al. 1992].
4.3 Electronegativity

Electronegativity, $\chi$, the ability of an atom to attract electron density towards itself within a covalent bond, correlates with many chemical properties, e.g. IR stretching frequencies, NMR chemical shifts and Mössbauer isomer shifts. It cannot be measured directly, and is calculated from other atomic / molecular properties, e.g.:

- Pauling (A-A, A-B and B-B bond energies) [Pauling 1932]
- Mulliken (arithmetic mean of IP & EA) [Mulliken 1934; Mulliken 1935]

Discussion of bond polarity relies upon $\chi$, with ionic bonds being formed if $\Delta \chi > 0$. By placing haptic springs (Section 4.1) with spring constant $\propto \chi$ at each atomic center, the effects of bond polarity can be haptically described for a series of homo- and heteroatomic halogen-containing diatomics. For ionic NaCl, only two springs are felt, whilst an additional (non-scripted) haptic minimum can be located in the middle of the Cl-Cl bond for non-polar Cl$_2$ (Figure 9). The effect of polarity upon the position of this additional haptic minimum (covalent compounds only) is depicted for hydrogen halides, where the position of the minimum shifts towards the electronegative halogen with increasing bond polarity (Figure 10).

5 Acidity and Basicity

Lewis acids (electrophiles) and bases (nucleophiles) are electron-pair acceptors and donors: A + :B → A-B. Lone electron pairs from the highest occupied molecular orbital (HOMO) of the base is donated to the electron-deficient lowest unoccupied molecular orbital (LUMO) of the acid via a coordinate covalent bond. Brønsted-Lowry theory: acid (AH) + base (B) ⇌ conjugate base (A$^-$) + conjugate acid (BH$^+$), however, deports acids and bases as proton donors and acceptors. The two theories are distinct but complementary, since a Lewis base is a Brønsted-Lowry base, but a Lewis acid need not be a Brønsted-Lowry acid. A quantitative measure of acid strength ($HA \rightarrow A^- + H^+$) in (usually aqueous) solution is the acid dissociation constant, $K_a$, where $K_a = \frac{[A^-][H^+]}{[HA]}$. A logarithmic measure of the acid dissociation constant, $pK_a = -\log_{10} K_a$ is more commonly employed. For a diatomic molecule with masses $m_1$ and $m_2$, the vibrational frequency, $\nu$ is given by:

\[
\nu = \frac{1}{2\pi c} \sqrt{\frac{c}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}
\]

Calculation of force constants, $k$, for a polyatomic molecule from its vibrational frequencies is difficult as the number of force constants, including coupling between normal modes, can exceed the number of fundamental modes. Even for water, the equations describing the force constants are complex. The highlighted bond can be approximated by a simple harmonic oscillator, with functional groups on either side of the bond described by single entities.

In order to investigate some of the factors which might affect acidity, the orbital energy (eigenvalue) of the highest occupied molecular orbital (HOMO), $E_H$, and the O–H vibrational frequency, $\nu$, were calculated for a training set of organic carboxylic acids and alcohols using semi-empricial quantum mechanical calculations (AM1, PM3, PM6, see Table 8). PM6 results have been omitted from Table 8 since the predicted O–H stretching frequencies were unrealistic (1000 cm$^{-1}$ too low).

Strong correlations ($r^2 = 0.97$) were found between $\nu$ and pKa for the AM1 semi-empricial method whilst the correlation against $E_H$ was much weaker ($r^2 = 0.48$). Correlations between $\nu$, $E_H$ and pKa are very much weaker for the reparameterised PM3 and PM6 methods ($r^2 = 0.50$ (neglecting PM3 outlier for X=H, otherwise 0.06), and 0.67 for PM6). The vibrational frequency, $\nu$, is not only dependent upon the force constant, $k$, but also upon the reduced mass $\mu$. High correlations ($r^2 = 1$ and 0.97) are obtained between $k_2$ (mean $\mu$) and both $\nu$ and pKa respectively. Correlation between $k_1$ (variable $\mu$) and both $\nu$ and pKa, however, remain significant ($r^2 = 0.78$ and 0.77 respectively).
Table 8: Correlation of acid strength, pKa, against semi-empirical HOMO energy (\(E_H, \text{eV}\)), O-H stretching frequency (\(\nu, \text{cm}^{-1}\)) and force constant \((k, \text{N m}^{-1})\)

<table>
<thead>
<tr>
<th>X-CO₂H</th>
<th>pKa</th>
<th>AM1</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_H)</td>
<td>(\nu)</td>
<td>(k_1)</td>
</tr>
<tr>
<td>CF₃</td>
<td>-0.25</td>
<td>-12.5</td>
<td>3393</td>
</tr>
<tr>
<td>CCl₃</td>
<td>0.65</td>
<td>-12.0</td>
<td>3401</td>
</tr>
<tr>
<td>CH₃₂</td>
<td>1.29</td>
<td>-11.7</td>
<td>3415</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>1.68</td>
<td>-12.3</td>
<td>3406</td>
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<td>n-NO₂Ph</td>
<td>2.17</td>
<td>-11.9</td>
<td>3414</td>
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<td>m-NO₂Ph</td>
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<td>3417</td>
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<td>CH₃F</td>
<td>2.66</td>
<td>-11.7</td>
<td>3422</td>
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<tr>
<td>CH₃Br</td>
<td>2.86</td>
<td>-11.3</td>
<td>3421</td>
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<tr>
<td>CH₃Cl</td>
<td>2.86</td>
<td>-11.6</td>
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<tr>
<td>o-CIPh</td>
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<td>3427</td>
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<td>CH₃I</td>
<td>3.12</td>
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<td>p-NO₂Ph</td>
<td>3.44</td>
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<td>H</td>
<td>3.77</td>
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<tr>
<td>m-CIPh</td>
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<tr>
<td>Ph</td>
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<tr>
<td>CH₃=CH</td>
<td>4.25</td>
<td>-11.5</td>
<td>3429</td>
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<tr>
<td>CH₂</td>
<td>4.76</td>
<td>-11.6</td>
<td>3432</td>
</tr>
<tr>
<td>PhOH</td>
<td>9.95</td>
<td>-9.1</td>
<td>3461</td>
</tr>
<tr>
<td>MeOH</td>
<td>15.50</td>
<td>-11.1</td>
<td>3502</td>
</tr>
</tbody>
</table>

Force constants, \(k_1\) and \(k_2\) (ideal), can be incorporated into a haptic model for Lewis acidity, where acidic proton is the haptic probe. The O–H force-constants are similar (as expected); nevertheless, acids with smaller \(k_0=-H\) (and smaller pKa) exhibit weaker O–H bonds and labile, acidic protons. Construction of this application and associated lesson plan is currently underway. Such a lesson would involve the symbiotic use of quantum mechanical calculations and haptics to probe not only acidity but also to investigate the affect of isotopic substitution upon the vibrational frequency. The generality of the approach will be investigated for a variety of organics containing different functional groups, X–H (X = B, C, N, O, S), with a predicted profound affect upon the vibrational frequencies, force constants and proton acidity.

### 5.1 Chemical Hardness

Further classification into Hard (high charge, weakly polarizable) and Soft (low charge, strongly polarizable) Acids and Bases (HSAB theory) can be performed, where hard (soft) acids & bases possess:

- **small** (large) atomic / ionic radii
- **high** (low or zero) oxidation state
- **low** (high) polarizability
- **high** (low) electronegativity
- **low** (high) - energy HOMO (bases)
- **or** (and) high (low)- energy LUMO (acids)

Hard acid - hard base interactions (ionogenic, enthalpy favoured) and soft acid - soft base interactions (covalent character, entropy favoured) are stronger than hard acid - soft base or soft acid - hard base interactions. HSAB theory provides a qualitative, rather than quantitative description of predominant factors which drive chemical properties and reactions, such as relative ordering of ligands and transition metal ions in terms of their hardness and softness, e.g. poisoning of metals in catalytic converters by soft bases such as sulfides. The sensitivity and performance of explosive materials can also be explained on basis of HSAB theory.

A quantitative [Parr and Pearson 1983; Pearson 1988b; Zhan et al. 2003; Pearson 2005] extension of HSAB theory employs the chemical hardness (\(\eta\)) which is proportional to the band gap:

\[
\eta = \left( \frac{1}{2} \frac{\partial^2 E}{\partial N^2} \right)_z = \left( \frac{1}{2} \frac{\partial \mu}{\partial N} \right)_z \approx \left( -\frac{1}{2} \frac{\partial \chi}{\partial N} \right)_z
\]

\[
\chi = -\mu - \frac{1}{2} (IP + EA)
\]

Costly, but accurate, vertical IPs and EAs can be calculated from the relative energies, \(E\), of neutral \(M\) and \(M^+\), \(M^-\) ionic systems:

\[
IP = E_{M^+} - E_M, \quad EA = E_M - E_{M^-}
\]

Using the simpler Koopmans’ theorem [Koopmans 1934; Cederbaum and Domcke 1977]:

\[
\eta = \frac{E_L + E_H}{2}, \quad \chi = -\frac{E_L + E_H}{2}
\]

Although Koopmans’ theorem produces too positive ionization potentials and too negative electron affinities, chemical hardness, \(\eta\), values predicted using Hartree-Fock methods are in excellent agreement [Kolandaivel and Jayakumar 2000; Padmanabhan et al. 2005; Senthilkumar and Kolandaivel 2002], since the omission of electron correlation cancels the relaxation error for IP, but not for EA [Szabo and Ostlund 1996]. Density functional theory (DFT) calculations require a simple correction [Tozer and DeProft 2005], based upon an experimental ionization potential, IP, where the error is cancelled due to opposite shifting of HOMO and LUMO energies.

\[
\eta = \frac{E_L + E_H}{2}, \quad \chi = -\frac{E_L + E_H}{2}
\]

Orbital energies calculated using quantum mechanical (semi-empirical, Density Functional Theories (DFT)) methodologies allows the prediction of chemical hardness, \(\eta\) (Table 9). A haptic CPK atom can be represented using a sphere whose haptic surface is described by a SmoothSurface node within the sphere’s Appearance node. Modification of stiffness and velocity based damping SFFloat fields of the SmoothSurface node should allow a qualitative description of polarizability (\(\alpha\)) based upon the chemical hardness, \(\eta\), with low and high \(\alpha\) producing hard and spongy atoms respectively. Although stiffness values range from 0 to 1, a minimal amount of stiffness is required to haptically probe the atom, with semi-quantitative predictions only for large \(\Delta \alpha\).

### 6 Future Work

Initial proof-of-concept methodologies are presented in this paper. Completed user interfaces will be demonstrated to lecturers, teachers and students allowing a thorough evaluation of the effectiveness (and any subsequent modification) of the haptic user interface. Lesson plans adapted for both university and secondary level will also be created to gauge the benefits of the haptic approach over standard teaching methodologies. The extensibility and ease of programming of H3D/X3D will also allow the rapid development of a bilingual (Welsh / English) user interface.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Expt</th>
<th>AM1</th>
<th>PM3</th>
<th>PM6</th>
<th>DFT/TNP</th>
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<tbody>
<tr>
<td></td>
<td>IP</td>
<td>EA</td>
<td>$\eta$</td>
<td>$E_H$</td>
<td>$E_L$</td>
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<td>-14.1</td>
<td>6.7</td>
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<tr>
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<td>-7.8</td>
<td>10.3</td>
<td>-13.3</td>
<td>4.7</td>
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<tr>
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<td>4.4</td>
</tr>
<tr>
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<td>-2.2</td>
<td>8.9</td>
<td>-14.3</td>
<td>1.0</td>
</tr>
<tr>
<td>HCl</td>
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<td>-3.3</td>
<td>8.0</td>
<td>-12.3</td>
<td>1.9</td>
</tr>
<tr>
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<td>-1.8</td>
<td>7.9</td>
<td>-13.3</td>
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</tr>
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<td>7.5</td>
<td>-11.3</td>
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<tr>
<td>F$_2$</td>
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<td>-1.2</td>
<td>7.2</td>
<td>-14.3</td>
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<td>CH$_2$O</td>
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<td>-10.8</td>
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<td>1.0</td>
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<td>-1.1</td>
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<tr>
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<td>0.0</td>
<td>5.2</td>
<td>-11.6</td>
<td>-1.1</td>
</tr>
</tbody>
</table>

$^{2}\chi$ 0.94 0.87 0.86 0.89 0.97

7 Conclusions

Two different approaches for the preparation of novel cost-effective molecular haptic applications based upon a H3D viewer & a Novint Falcon have been developed, allowing haptics perception of key chemical concepts, e.g. reactivity, periodicity and acidity taught at both secondary and undergraduate levels. The first approach utilises Perl scripting within a commercial molecular modelling suite to efficiently generate a H3D scene graph for haptic perception of CPK space-filling atoms. Static or animated systems can be post-visualized using a H3D viewer. Within the second approach, prototype H3D user interfaces are created, where key data may be obtained from literature or quantum mechanical calculations.

Initial feedback indicates that the haptic approach is ideally suited for pupils with high practical aptitudes and would complement traditional mathematical-based teaching methods. At undergraduate level, the lesson plans (in development) would symbiotically merge haptics with simulations, allowing a student to generate & incorporate data e.g. molecular geometry, force constants, orbital eigenvalues, atomic charges etc. into the H3D file, allowing qualitative predictions for unknown systems. Simpler lesson plans would be introduced for secondary school education.

References


