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Electrostatics at the Molecular Level

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Abstract

In molecular systems, positive and negative charges are separated, making them ideal systems to examine electrostatic interactions. The attractive force between positive and negative charges is balanced by repulsive 'forces' that are quantum-mechanical in origin. We introduce an 'effective' potential energy that captures the repulsion; it allows us to obtain fairly accurate estimates of the bonding properties of molecular systems. We use units (e.g., kcal mol^{-1} for energy) that emphasize the relevance of electrostatics to macroscopic behavior.

Keywords: electrostatics, chemical bond, thermal properties of matter

1. Introduction

The *Next Generation Science Standards* [1] that emphasizes finding solutions to *real-world* problems. In the standard MS-PS1-1, students are expected to 'develop models to describe the atomic composition of simple molecules and extended structures. Emphasis is on developing models of molecules that vary in complexity. Examples of simple molecules could include ammonia and methanol. Examples of extended structures could include sodium chloride or diamonds. Examples of molecular-level models could include drawings, 3D ball and stick structures, or computer representations showing different molecules with different types of atoms'.

In fact, many students, especially those in the algebra-based sequence, are first introduced to electric charges and the forces between them in a general chemistry course when the bonding of atoms in molecules is discussed. Molecular systems are compelling examples for electrostatics because Coulomb forces are dominant on the scale of *nanometers* and below. This is not the case on the scale of *centimeters* and longer, where the Coulomb force is often a 'curiosity' (e.g., 'clinging' of clothes taken from a dryer), although electric forces are *billion–billion–billion–billion* times stronger than gravitational forces, as Feynman points out [2]. Electric force goes largely unnoticed in every day life because the positive and negative charges are perfectly balanced. The fact that electrons and protons are kept in roughly the

same places explains the rigidity of macroscopic material: for example, the 440 m Willis Tower in Chicago swings only about 1 m in a strong storm [3].

Physical theories should be illustrated with examples of realistic systems so that students can develop a 'sense' of numbers. The author of recent article in *The Physics Teacher* [4] discusses why this is a challenge for electrostatics. This explains why in many textbook problems, one encounters electric fields between charged objects that exceeds the breakdown value for air (3×10^6 N C^{-1}), while in other cases, the electric charge is unreasonably high (e.g., higher than the 7 μC-charge of a 450 kV Van de Graff). The author proposes that values of electrostatics problems should be 'those that are readily achieved in laboratory and classroom situations'. Known examples are (party-) balloons, pith balls, styrofoam peanuts, and electroscopes.

However, it is only difficult to find macroscopic examples of electrostatics if we restrict ourselves to few-particle systems, similar to mechanical systems, but 'the phenomena we commonly observe involve not two or three but of the order of 10^{27} particles' [5]. For example, the latent heat of fusion of water (H_2O) $L_f = 6.04$ kJ mol^{-1} is related to molecular properties via Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1} so that $\epsilon = L_f/N_A = 1.0 \times 10^{-20}$ J. This calculation suggests that molecular systems can be used to illustrate the principles of electrostatics; students 'make sense of numbers' by relating the results to a macroscopic behavior of matter [4].

The description of electrons in molecules requires, of course, a quantum mechanical treatment, and we refer the reader to [6] for a rather complete treatment in the case of small molecules. Two main features emerge from such a treatment: (1) the electrons is shared by the atoms in a molecule, i.e., there is a finite probability for any electron to be near any atom, so that the 'effective' charge of an atom is a fraction of an elementary charge and can be negative or positive; we say that atoms have *partial charges*. (2) There is a repulsive force between atoms and molecules at short distances and essentially has quantum mechanical origin: (i) When electron shells overlap, the atomic nuclei are no longer shielded and repel each other. (ii) Electrons with the same spin repel each other due to the Pauli exclusion principle when their orbitals overlap [7]. As a result, attractive Coulomb forces are balanced by repulsive forces, which explains the stability of molecules and, in particular the equilibrium lengths of bonds.

We develop a simple model of the rigidity of the OH-bond of a water molecule H_2O and the hydrogen bonding of a water dimer. We use known values for the partial charges of hydrogen and oxygen atoms in a water molecule. We treat the repulsion between atoms by introducing a phenomenological potential that decays exponentially with the distance between atoms. Phenomenological models play an important role as they provide 'a quick practical way to form simple pictures and rough estimates of properties whose more precise comprehension may require analysis of considerable complexity' [8].

The outline of the paper is as follows. We discuss the relevant scales of the energy and force at the molecular level in section 2. We examine the intramolecular force of the OH-bond in a water molecule in section 3, and obtain the repulsive forces between oxygen and hydrogen from the vibrational properties of the OH-bond; we calculate the force from Coulomb's law, rather than from the derivative of the electrostatic potential energy, to make a clear connection to introductory physics. We discuss the intermolecular force between molecules in a water dimer in section 4; we use a simple argument to find the net attraction between oxygen and hydrogen atoms responsible for hydrogen bonding. We then find the bonding energy of hydrogen bond and its vibrational property. We relate the *intra-* and *inter-* molecular binding energies to thermal properties of water. We summarize our results in

section 5, and discuss some implications for the teaching of electrostatics in the algebra-based introductory physics.

2. Energy scales

The force between two charges q_1 and q_2 separated by the distance r is given by Coulomb's law $F = (4\pi\epsilon_0)^{-1}q_1q_2/r^2$, and the corresponding potential energy is $EPE = (4\pi\epsilon_0)^{-1}q_1q_2/r$, with $(4\pi\epsilon_0)^{-1} = 9.0 \times 10^9\,\text{Nm}^2\,\text{C}^{-2}$. The appropriate length scale for atoms and molecules is one Ångstrom:

$$\mathcal{L} = 1.0 \times 10^{-10}\,\text{m} = 100\,\text{pm}. \tag{1}$$

This length scale defines the energy scale $\mathcal{U} = (4\pi\epsilon_0)^{-1}e^2/\mathcal{L} = 2.3 \times 10^{-18}\,\text{J}$. In the context of chemistry and biology, (reaction) energies are often expressed in units of kcal mol^{-1}: 1 kcal mol^{-1} corresponds to $7.0 \times 10^{-21}\,\text{J}$ per atom or molecule. We write

$$\mathcal{U} = 330\,\text{kcal mol}^{-1}. \tag{2}$$

We compare this energy with other relevant energies. The latent heat characterizes the 'chemical energy' of matter. The values for water are $L_f = 1.44\,\text{kcal mol}^{-1} = 0.0044\,\mathcal{U}$ (fusion) and $L_v = 9.72\,\text{kcal mol}^{-1} = 0.092\,\mathcal{U}$ (vaporization), and are thus much smaller than $\mathcal{U}$.

The thermal energy is determined by the Boltzmann constant is $k_B T = 1.38 \times 10^{-23}\,\text{J K}^{-1}$

$$k_B = 0.002\,\text{kcal mol}^{-1}\,\text{K}^{-1}. \tag{3}$$

We calculate the corresponding temperature $T_\mathcal{U} = \mathcal{U}/k_B = 1.6 \times 10^5\,\text{K}$, which shows that $\mathcal{U}$ is an enormous energy for atomic and molecular systems.

Similarly, we define a characteristic force from Coulomb's law $\mathcal{F} = (4\pi\epsilon_0)^{-1}e^2/\mathcal{L}^2$, or

$$\mathcal{F} = 330\,\text{kcal mol}^{-1}\,\text{Å}^{-1}. \tag{4}$$

A typical *external* electric field is $E_0 = 1000\,\text{V m}^{-1}$ so that $eE_0 = 7.0 \times 10^{-9}\,\text{kcal (mol Å)}^{-1}$. We write $E = E'E_0$ and thus find the force on a partial charge δq in the electric field E':

$$F = 7.0 \times 10^{-9}\,\text{kcal mol}^{-1}\,\text{Å}^{-1}\,E'\,\delta q. \tag{5}$$

We find an upper bound of the scaled electric field from the the (average) intensity of a typical (industrial) solid-state laser $S = 3 \times 10^8\,\text{W m}^{-2}$
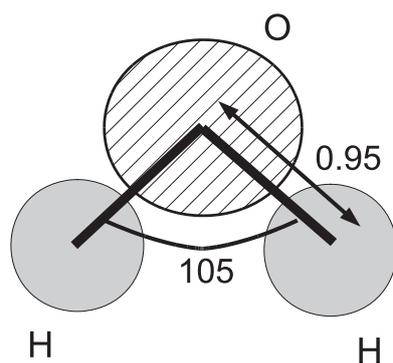
$$E'_{\text{max}} = 300. \tag{6}$$

The maximum external force on a charge follows $F_{\text{max}} = 2.1 \times 10^{-6}\,\text{kcal (mol Å)}^{-1}$, which is about six orders of magnitude smaller than the characteristic force $\mathcal{F}$.

We introduce scaled variables. We write the distance $d = \mathcal{L}d'$, and drop the prime in the following. The potential energy follows

$$EPE(r) = 330\,\text{kcal mol}^{-1}\frac{\delta q_1\,\delta q_2}{r} \tag{7}$$

and similarly the force:

$$F = 330\,\text{kcal mol}^{-1}\,\text{Å}^{-1}\frac{\delta q_1\,\delta q_2}{r^2}. \tag{8}$$

Figure 1. The model of a water molecule. The equilibrium length of the OH-bond is $l_0 = 0.95$ and the angle between the bonds is $105°$.

3. Intramoleculer forces

The (covalent) atomic radii of hydrogen and oxygen are found $R_H = 0.25$ and $R_O = 0.6$; the partial charges are[1] $\delta q_H = +0.4$ and $\delta q_O = -0.8$ [9]. The equilibrium distance OH in a water molecule is $l_0 = 0.95$, and the angle between the two OH bonds is $105°$, cf figure 1. The electrostatic interaction between oxygen and hydrogen follows

$$\text{EPE}(r) = -100 \text{ kcal mol}^{-1} \frac{1}{r}. \tag{9}$$

We ignore the motion of the oxygen atom since the oxygen atom is much heavier than the hydrogen atom.

   The properties of the OH-bond is determined by the electrostatic interactions and the repulsive force between charges. The net force explains the equilibrium length and the deviation from equilibrium give rise to an 'effective' elastic behavior of the OH-bond. Here, we start from known elastic properties of the bond and derive the properties of the repulsive potential between the oxygen and hydrogen atom. The vibrational frequency of the OH-bond is known from infrared (IR) spectroscopy, $f \simeq 1 \times 10^{14}$ Hz (derived from the wave number $\tilde{\nu}_1 = 3657 \text{ cm}^{-1}$ of the symmetric stretch [11]). The ratio of the spring constant k and the mass of a hydrogen atom $m = 1.67 \times 10^{-27}$ kg determines the angular frequency so that the spring constant follows $k = m\omega^2 \simeq 700$ N m^{-1}. Since $k\mathcal{L} = 7 \times 10^{-8}$ N, we find the spring constant in atomistic units

$$k \simeq 1000 \text{ kcal mol}^{-1} (\text{Å})^{-2}. \tag{10}$$

   The vibrational properties implies a harmonic approximation of the intramolecular potential of the OH-bond

$$U_{\text{intra}}(r) = U_{\text{min}} + \frac{1}{2} 1000 \text{ kcal mol}^{-1} (r - l_0)^2. \tag{11}$$

The potential U_{intra} is the sum of electrostatic potential energy EPE and the repulsion U_r between O- and H-atoms:

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[1] Partial, or atomic, charges are determined both experimentally and computationally. Different theoretical models yield values that differ significantly. We refer the reader to [9] for a detailed discussion of the various computational methods.
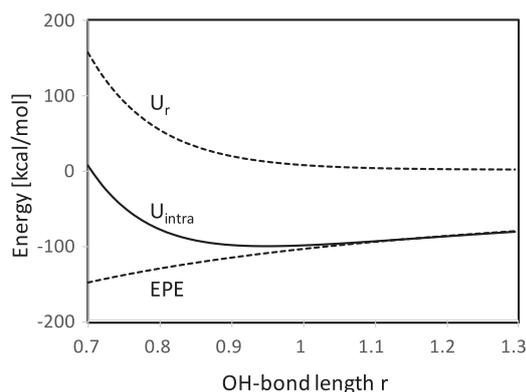
Figure 2. The electrostatic potential energy (EPE), repulsive potential (U_r), and intramolecular energy (U_{intra}) as a function of the OH-bond length.
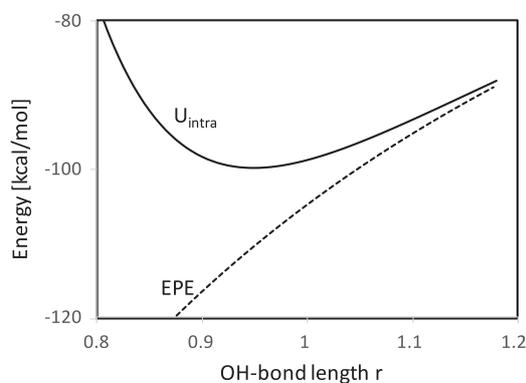
Figure 3. The electrostatic potential energy (EPE), and intramolecular potential (U_{intra}) as a function of the OH-bond length.

$$U_{intra}(r) = \text{EPE}(r) + U_r(r). \tag{12}$$

We assume exponential behavior

$$U_r(r) = U_0 e^{-\kappa r}. \tag{13}$$

We determine the constant U_0 and κ from first and second derivatives at the equilibrium distance l_0 $dU_{intra}/dr|_{l_0} = 0$ and $d^2 U_{intra}/dr^2|_{l_0} = 1000$ kcal mol^{-1}, and obtain

$$\kappa = 10.7 \tag{14}$$

and

$$U_0 = 2.8 \times 10^5 \, \text{kcal mol}^{-1}. \tag{15}$$

Thus, the strength of the repulsion is much larger than that of the Coulomb force $U_0 \gg \mathcal{U}$, but acts only over a very small range, $\delta r \simeq 1/\kappa = 0.1$. The exponential behavior of the repulsion between O- and H-atoms is only an approximation, and we expect that the constants depend on the distance r, $U_0 = U_0(r)$ and $\kappa = \kappa(r)$.
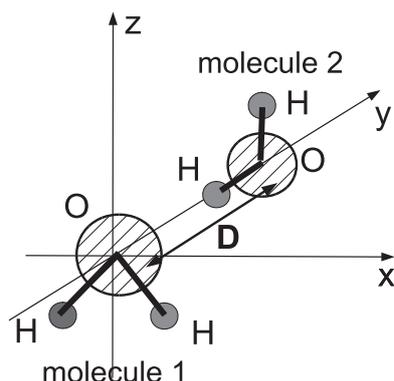
Figure 4. A simplified model of a water dimer; the angle between the OH-bonds is 90° and the OH-bond length is 1. The molecules 1 and 2 are in the (x, z)- and (y, z)-planes, respectively. The OO-distance is D.

The electrostatic potential energy EPE, the repulsive potential U_r, and the total energy U_{intra} of the OH-bond are shown in figure 2; the electrostatic potential energy EPE and the total energy U_{intra} of the OH-bond are shown in greater detail in figure 3. We direct the reader's attention to the narrow range of the OH-bond length, which is necessary since the repulsive potential becomes much larger at smaller distances, e.g., $U_r(0.5) \simeq$ 1300 kcal mol^{-1}. In figure 4, we plot the electrostatic potential energy EPE and the intramolecular potential U_{intra} over a smaller range of bond length. We find the minimum energy of the OH-bond $U_{min} = -100$ kcal mol^{-1}.

We assume that the water molecule is placed in a region with electric field E_{max}. Because the oxygen and hydrogen are pulled in opposite directions, we use $\delta q = 1.2$ and find from equation (5): $F = 2.5 \times 10^{-6} = 1000 \cdot \delta r$ and find that the OH-bond is stretched negligibly, $\delta r = 2.5 \times 10^{-9}$. Thus, an external force excites the OH-bond only if it is applied periodically with a frequency that corresponds to the natural frequency ω of the bond, which is the case when water is placed in a microwave oven. The strong frequency dependence is evident in transmission of light: a jar of water is nearly transparent when viewed with visible light (frequency range 4×10^{14} Hz $< f_{vis} < 8 \times 10^{14}$ Hz) but is opaque when viewed with microwaves (frequency $f_{micro} \simeq 1 \times 10^{11}$ Hz).

Water dissociates (i.e., the OH-bond breaks) when the temperature is a few thousand kelvin; we use[2] $T_{dissoc} \simeq 3000$ K [10]. The corresponding thermal energy follows $\Delta U_{dissoc} = k_B T_{dissoc} = 6$ kcal mol^{-1}. We set the dissociation energy equal to the elastic energy of the OH-bond: $6 = 1000(\Delta r)^2/2$, and find $\Delta r = 0.08$. The value is consistent with the Lindemann criterion[3] $\Delta r/l_0 \simeq 0.1$. We note that the variations of the bond lengths are much smaller than length scale associated with repulsive potential, $\delta r, \Delta r < 1/\kappa$, as it should be for consistency of the assumed exponential behavior of the repulsive potential.

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[2] More precisely, the fraction of dissociated water molecules increases as temperature increases. At 3000 K, the fraction is 11%, see, [10].
[3] This estimate is consistent with the Lindemann criterion for melting who proposed that melting occurs when the amplitude of the vibrations exceeds 10% of the atomic spacing. See, e.g., [7], p 268.

4. Intermolecular forces

We turn to intermolecular interaction and discuss the hydrogen bond of a water dimer. We simplify the water molecules and assume that the two OH-bonds make a right angle and assume that the equilibrium bond length is $l_0 = 1$. The geometry is shown in figure 4. We use coordinate systems (x, y, z) such that molecule 1 is in the (x, z)-plane. The oxygen atom is at the origin $\vec{r}_O = (0, 0, 0)$ and the hydrogen atoms: $\vec{r}_{H\pm} = (\pm 1/\sqrt{2}, 0, -1/\sqrt{2})$. Molecule 2 is in the (y, z)-plane. We use $D > 1$ for the distance between the oxygen atoms. The oxygen atom of molecule 2 is at $\vec{r}'_O = (0, D, 0)$, the bonded hydrogen at $\vec{r}'_{Hb} = (0, D - 1, 0)$, and the unbonded hydrogen at $\vec{r}'_{Hu} = (0, D, 1)$. The empirical value of the OO distance is $L_0 = 2.95$.

We calculate the force on a unit charge $\delta q = 1$ at $\vec{r} = (0, y, z)$ due to the charges on molecule 1. We calculate the y-component of force f_y: the contribution of the oxygen atom

$$f_{O,y} = -264 \text{ kcal mol}^{-1} \text{Å}^{-1} \frac{y}{[y^2 + z^2]^{3/2}} \tag{16}$$

and the contributions of the two hydrogen atoms:

$$f_{H,y} = 264 \text{ kcal mol}^{-1} \text{Å}^{-1} \frac{y}{[1/2 + y^2 + (z + 1/\sqrt{2})^2]^{3/2}}. \tag{17}$$

The total force follows $f_y = f_{O,y} + f_{H,y}$, or

$$f_y(y, z) = 264 \text{ kcal mol}^{-1} \text{Å}^{-1}$$
$$\times \left\{ \frac{y}{[1/2 + y^2 + (z + 1/\sqrt{2})^2]^{3/2}} - \frac{y}{[y^2 + z^2]^{3/2}} \right\}. \tag{18}$$

We now calculate the force on molecule 2 due to molecule 1. The contribution of the oxygen atom:

$$F_{O,y}(D) = -211 \text{ kcal mol}^{-1} \text{Å}^{-1} \left\{ \frac{D}{[D^2 + 1]^{3/2}} - \frac{1}{D^2} \right\}, \tag{19}$$

the contribution of the bonded hydrogen atom:

$$F_{Hb,y}(D) = 105.5 \text{ kcal mol}^{-1} \text{Å}^{-1} \left\{ \frac{D - 1}{[(D - 1)^2 + 1]^{3/2}} - \frac{1}{(D - 1)^2} \right\} \tag{20}$$
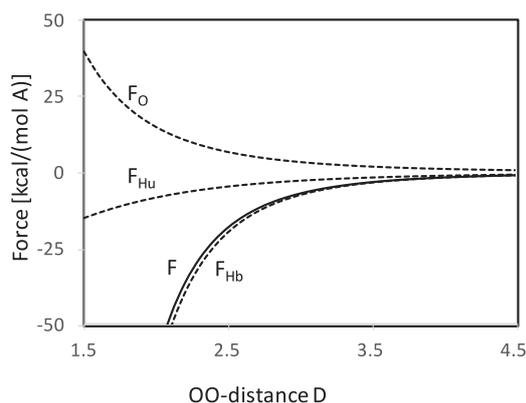
and the contribution of the unbonded hydrogen atom:

$$F_{Hu,y}(D) = 105.5 \text{ kcal mol}^{-1} \text{Å}^{-1} \left\{ \frac{D}{[1/2 + D^2 + (1 + 1/\sqrt{2})^2]^{3/2}} - \frac{D}{[D^2 + 1]^{3/2}} \right\}. \tag{21}$$

The electrostatic force between the water molecules along the y-axis follows

$$F_y(D) = F_{O,y}(D) + F_{Hb,y}(D) + F_{Hu,y}(D). \tag{22}$$

The forces $F_{O,y}$, $F_{Hb,y}$, $F_{Hu,y}$, and F_y as a function of the OO-distance are shown in figure 5. We conclude that the forces exerted on the oxygen atom and the unbonded hydrogen atom approximately cancel out each other; and the force between the two water molecules is largely due to the bonded hydrogen atom.

We plot $\log(|F_y|)$ versus $\log(D)$ in figure 6; the slope of the dashed line is 5 and the intercept is 7.8. We find the power-law behavior of the attractive force induced by the

Figure 5. The electrostatic force along the *y*-axis on the oxygen atom (O), bonded hydrogen atom (Hb), unbonded hydrogen atom (Hu) (all dashed), and the net electrostatic force along (solid) as a function of the OO-distance *D*.
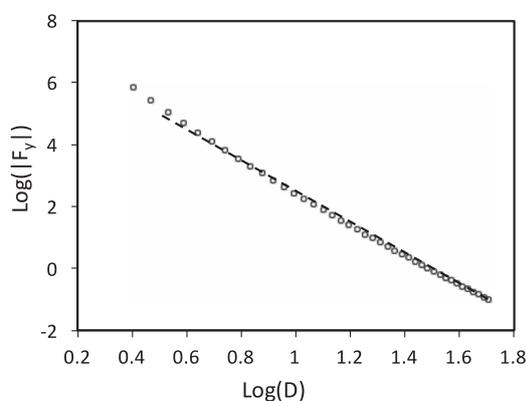

Figure 6. The net force along the *y*-axis as function of the OO-distance in a double-logarithmic plot; the dashed line has slope 5 and intercept 7.8.

hydrogen bond for $D > D_c = 2$:

$$F_y(D) \simeq -52 \text{ kcal mol}^{-1} \text{ Å}^{-1} \left(\frac{D_c}{D}\right)^5, \quad D > D_c. \tag{23}$$

We conclude that the attractive electrostatic interaction between the two water molecules in a water molecule decays faster than the inverse-square dependence Coulomb's law, which reflects the electrically neutral character of water molecules. We emphasize that the exponent $n = 5$ is not universal and applies only to the particular geometry of the dimer. The prefactors in equations (8) and (23) are of the same order (330 kcal (mol Å)$^{-1}$ versus 52 kcal (mol Å)$^{-1}$) so that the strengths of the forces are similar. We obtain the attractive Coulomb force between the water molecules near the equilibrium distance L_0, $F_{C,y}(L_0) \simeq -6.8$ kcal (mol Å)$^{-1}$.

We find the electrostatic potential energy of a unit charge $\delta q = 1$ at $\vec{r} = (0, y, z)$ in the electric field produced by the water molecule 1. The contribution of the oxygen atom:
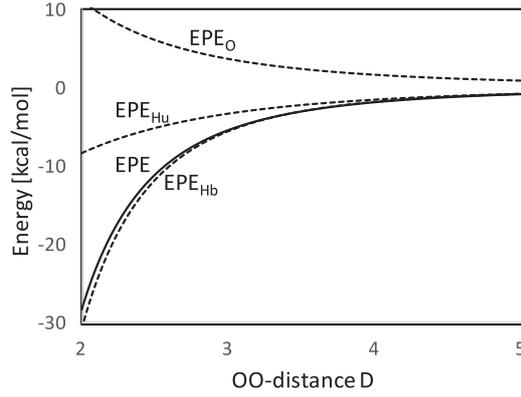
Figure 7. The electrostatic potential of the oxygen atom (O), bonded hydrogen atom (Hb), unbonded hydrogen atom (Hu) (all dashed), and the total electrostatic potential energy as a function of the OO-distance D.

$$u_O = -264 \text{ kcal mol}^{-1} \frac{1}{\sqrt{y^2 + z^2}} \tag{24}$$

and the two hydrogen atoms:

$$u_H = 264 \text{ kcal mol}^{-1} \frac{1}{\sqrt{1/2 + y^2 + (z + 1/\sqrt{2})^2}}. \tag{25}$$

The total electrostatic potential energy $u_O + u_H$ follows

$$u = 264 \text{ kcal mol}^{-1} \left\{ \frac{1}{\sqrt{1/2 + y^2 + (z + 1/\sqrt{2})^2}} - \frac{1}{\sqrt{y^2 + z^2}} \right\}. \tag{26}$$

We now calculate the electrostatic potential energy of the water molecule 2 in the electric field produced by molecule 1. The contribution of the oxygen atom:

$$EPE_O = -211 \text{ kcal mol}^{-1} \left\{ \frac{1}{[1 + D^2]^{1/2}} - \frac{1}{D} \right\}, \tag{27}$$

the bonded hydrogen:

$$EPE_{Hb} = 105.5 \text{ kcal mol}^{-1} \left\{ \frac{1}{[1 + (D-1)^2]^{1/2}} - \frac{1}{D-1} \right\} \tag{28}$$

and the unbonded hydrogen:

$$EPE_{Hu} = 105.5 \text{ kcal mol}^{-1} \left\{ \frac{1}{[1/2 + D^2 + (1 + 1/\sqrt{2})^2]^{1/2}} - \frac{1}{[D^2 + 1]^{1/2}} \right\}. \tag{29}$$

The total potential energy of the electrostatic interaction between the two water molecules follows

$$EPE(D) = EPE_O(D) + EPE_{Hb}(D) + EPE_{Hu}(D). \tag{30}$$

We plot EPE_O, EPE_{Hb}, EPE_{Hu}, and EPE as a function of the OO-distance D in figure 7. We find that the total electrostatic potential energy is dominated by the potential energy of the bonded hydrogen atom, $EPE \simeq EPE_{Hb}$, which is, of course, consistent with the analogous
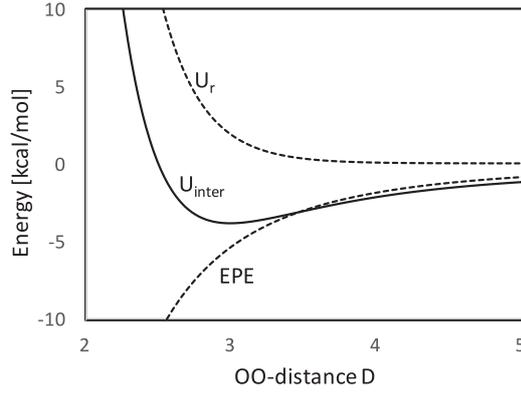
Figure 8. The total electrostatic potential energy EPE, the repulsive potential U_r, and the intermolecular energy U_{inter} as a function of the OO-distance.

property of the electrostatic force between water molecules. We find the electrostatic potential energy at the equilibrium distance L_0: $EPE(L_0) = -5.7$ kcal mol^{-1}.

We assume that the repulsion between the oxygen and hydrogen atoms of the hydrogen bond has exponential behavior, see equation (13)

$$U_r'(D) = U_0' e^{-\kappa' D}. \tag{31}$$

We expect that the repulsive potential is weaker at larger distances

$$U_0' = U_0 \frac{l_0}{L_0} = 9.1 \times 10^4 \tag{32}$$

and dependence on the distance is softer

$$\kappa' = \kappa \frac{l_0}{L_0} = 3.6. \tag{33}$$

The repulsive potential energy at the equilibrium distance follows $U_{ex}(L_0) = +2.2$ kcal mol^{-1}.

The intermolecular potential energy of the hydrogen bond in the water dimer follows

$$U_{inter}(D) = EPE(D) + U_r'(D). \tag{34}$$

We plot the electrostatic potential energy EPE, the repulsive potential between water molecules U_r', and the intermolecular energy U_{inter} as a function of the OO-distance in figure 8. We require that the equilibrium distance L_0 is the local minimum of the intermolecular potential. We find the repulsive force: $F_r(L_0) = -dU_r/dD|_{L_0} = +6.6$ kcal (mol Å)$^{-1}$. The net force follow $F_{total}(L_0) = F_{C,y}(L_0) + F_r(L_0) \simeq -6.8$ kcal (mol Å)$^{-1}$ + 6.6 kcal (mol Å)$^{-1}$ $\simeq 0$, as it should.

We find the repulsive potential at the equilibrium distance $U_r(L_0) = 2.2$ kcal mol^{-1} so that the inrermolecular potential has the minimum $U_{inter}(L_0) = -5.7$ kcal mol^{-1} + 2.2 kcal mol^{-1} so that

$$U_{min}' = -3.5 \text{ kcal mol}^{-1}. \tag{35}$$

This energy corresponds to the binding energy (or 'bond strength') of the hydrogen bond of the water dimer; a quantum-mechanical calculation yield $\Delta E_{H-bond} = 3.4$ kcal mol^{-1} [12]. Thus, our approximate theory gives a surprisingly accurate result, and validates our use of a phenomenological form for repulsion between charges.

We use a harmonic approximation of the intermolecular interaction

$$U_{\text{inter}}(D) = U'_{\text{min}} + \frac{1}{2}k'(D - L_0)^2.$$

The spring constant follows from the second derivative $k' = \mathrm{d}^2U_{\text{inter}}/\mathrm{d}D^2|_{L_0}$

$$k' \simeq 12 \text{ kcal mol}^{-1} (\text{Å})^{-2}. \tag{36}$$

We conclude that the *intra*-molecular OH-bond is much stiffer than the *inter*-molecular hydrogen bond.

We use the Lindemann criterion to find an estimate for the temperature when the water dimer breaks up. We find $\Delta D \simeq 0.1 L_0 = 0.3$ and find $\Delta U_{\text{inter}} \simeq (1/2)$ 12 kcal mol^{-1} $(0.3)^2 = 0.5$ kcal mol^{-1}. The corresponding temperature follows $T'_{\text{dissoc}} = \Delta U_{\text{inter}}/k_B = (0.5 \text{ kcal mol}^{-1})/[0.002 \text{ kcal (mol K)}^{-1}] = 250 \text{ K}$, or approximately the melting temperature of ice ($T_{\text{melt}} = 273 \text{ K}$). We point out that the rather accurate predicted value of the melting temperature of water is due to fortuitous choice of parameter, in particular the choice of partial charges of hydrogen and oxygen atoms. The result $T'_{\text{dissoc}} \simeq T_{\text{melt}}$ is consistent with the view that melting is associated with breaking of bonds between water molecules that give rise to formation of ice crystals.

5. Discussion

A recent paper in *The Physics Teacher* pointed out that macroscopic application of electrostatics generally necessitates that the system's parameters (mass, charge, size, etc) are fine-tuned. In fact, Coulomb forces are generally not noticeable at length scales of 1 cm or longer because macroscopic objects typically have zero net charge. In contrast, positive and negative charges are separated in molecules, which explains why Coulomb forces are dominant at the molecular level. While electrons must be described by the laws of quantum mechanics at lengths of molecules (*nano*-meter), we propose a phenomenological treatment in terms of partial charges and a repulsive potential.

The connection with the macroscopic world is then achieved by multiplying molecular interaction energies with Avogadro's number and calculate molar heat In this way, molecular systems are excellent examples to illustrate principles of electrostatics, since no 'fine-tuning' of parameters is necessary.

We discuss the properties of the OH-bond of a water molecule and the hydrogen bond of a water dimer, and showed that the description of the charge repulsion allows to derive properties of the molecular systems that are surprisingly close to their empirical values. We relate the properties of the intra- and inter-molecular forces to thermal properties of water.

A phenomenological treatment for the quantum-mechanical repulsion is key for our calculation, and we use empirical values of the OH- and hydrogen-bond lengths to find parameters that characterize this 'effective' potential. We are familiar with a similar situation from Newtonian mechanics, where the summation of small elastic compression forces between two objects (for example, two blocks) is treated as 'normal force.' There is no general expression for this force and its value is determined as part of the solution of the mechanical problem (the net force along a direction perpendicular to the contact surface must be zero).

An emphasis on 'chemical' problems is suitable in particular for the algebra-based sequence. Most students also take general and organic chemistry, as well as biochemistry, and are thus familiar with molecular models. While some of the calculations presented here are beyond the level of such a course, it is straightforward to simplify the mathematics (e.g., by

using graphical methods rather than calculus) to make it suitable for classroom use. The use of atomistic units (e.g., kcal mol^{-1} for energy) is particularly helpful to make connections with macroscopic properties.

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