JOURNAL OF CHEMICAL EDUCATION

Laboratory Experiment

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Computational Chemistry Laboratory: Calculating the Energy Content of Food Applied to a Real-Life Problem

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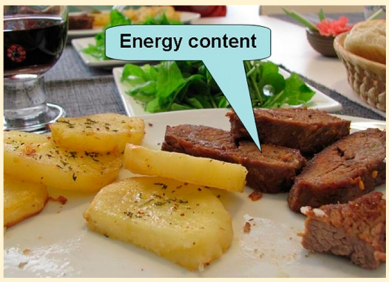
Supporting Information

ABSTRACT: In this laboratory, students calculated the nutritional value of common foods to assess the energy content needed to answer an everyday life application; for example, how many kilometers can an average person run with the energy provided by 100 g (3.5 oz) of beef? The optimized geometries and the formation enthalpies of the nutritional components of the food and their combustion products were calculated using molecular mechanics and a semiempirical method, AM1 or PM3, on the lab computers. These data were used to assess the energy content of common foods and compare with food label information. This general chemistry laboratory was designed for students of food engineering, yet it is applicable to students in any general chemistry course. Groups of students have successfully completed the laboratory as described here. The software was introduced, and the calculations were carried out in two, 2.5 h-long sessions.



KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Computer-Based Learning, Inquiry-Based/Discovery Learning, Computational Chemistry, Consumer Chemistry, Food Science, Industrial Chemistry, Molecular Modeling, Chemical Engineering*

INTRODUCTION

This laboratory is to introduce college students to computational molecular modeling techniques that will allow them to perform thermodynamic calculations related to nutrition. There are multiple advantages to engaging students in this way, such as the benefits of visualization in the comprehension of molecular-level phenomena,[1,2] the connection of the chemistry curriculum to real life issues,[3] and the preparation for a 21st century computer-rich work environment. The laboratory was developed for first year students taking chemistry for food science, human nutrition, and pharmacy majors, and it has also been used for standard general chemistry courses. College students are habitual users of digital technology,[4] so it should be easy to engage in computational chemistry with them.

Simulations carried out at the atomic level with quantum mechanical calculations start by giving the approximate structural molecular formula. These techniques allow the building of complex molecular images that can be enlarged or rotated in space (Figure 1), and the image of the molecule can be represented in different ways such as tubes with ribbons or balls and spokes[5,6] (Figure 2).

The calculations proposed are fast enough to be performed on several molecules of different size and form. It is thus possible to enhance understanding of several trends in families of structurally related molecules (in this lab: alanine, valine, leucine, iso-leucine).

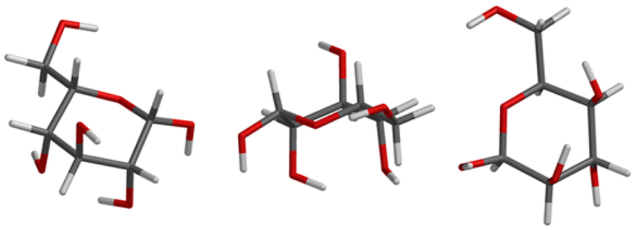


Figure 1. Glucose molecule visualized from different angles, modeled with tubes. PM3 calculation with Spartan.[19]

New editions of chemistry textbooks include food and nutrition responding to contemporary concerns about a healthy and balanced nutrition and its relation with chemistry.[7−9] Similarly, in celebration of the International Year of Chemistry (IYC2011), the Swedish Chemical Society chose two months to address food[10] to show the connection of chemistry with everyday life. In the laboratory presented here, students began by reading recent articles from popular sources, both to access up-to-date information on food or nutrition and to help them relate course content to each day life.[11] In addition, the assigned reading can promote interesting discussions in class among the students and with the instructor.

The field of computer simulation has been rapidly developing in chemistry: just in academic circles, a literature search (Web

dx.doi.org/10.1021/ed2008894 | J. Chem. Educ. XXXX, XXX, XXX−XXX

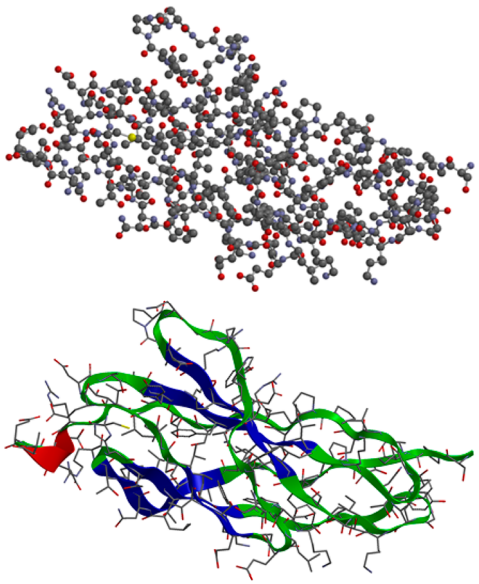


Figure 2. Partial visualization of the protein titin, with 1BPV code from the Protein Data Bank. (Top) Ball and spoke representation. (Bottom) Tube representation with ribbons. Both without H atoms and modeled with Spartan.[19]

of Science) using the keywords computational and chemistry led to more than 8000 references between the years 2000 and 2014. Simulations contribute to cutting edge research, both as computer experiments in themselves and in interpreting complex experimental data. The speed of technological progress is such that computational chemistry is being used more frequently in industries such as materials,[12] energy,[13] catalysis,[14] and drug discovery.[15] Especially in the latter, some industries are already turning toward molecular computations as a primary source of research and development.[16]

EXPERIMENTAL OVERVIEW

This exercise is based on a modification and extension of the exercise proposed by Caffery et al.[17] Students were introduced to the basic processes of releasing energy from food. They became familiarized with molecular modeling techniques and performed simple thermodynamic calculations. They calculated the energy released in the combustion of food items according to the food's composition in terms of carbohydrates, fats and proteins. As a starting point, carbohydrates are represented solely by glucose, fats are represented solely by stearin, and proteins are represented solely by a single amino acid or dipeptide. The chosen molecules require brief calculations which are recommended for students with no prior modeling experience. For the computational calculations performed in the lab, the degradation products of glucose and stearin were assumed to be CO_2 and H_2O and, in the case of proteins, urea, $(NH_2)_2CO$, CO_2, and H_2O. Students then were able to compare their results to packaging information on food items. Finally, questions like "How many kilometers can an average person run with the energy provided by 100 g of beef?" were answered by students based on their molecular modeling results and calculations.

BACKGROUND

A complete discussion of food energy values can be found in Brown et al.[9] and is summarized here. Food energy values can be measured with a bomb calorimeter. The heat flow, measured at constant volume, corresponds to the change in internal energy. Food containers and packages report this energy. The values informed for food items correspond to nutritional calories (Cal), equivalent to thermochemical kilocalories, that is, 1 Cal = 1000 cal = 4184 J.

The energy that our body needs comes mainly from the carbohydrates and from fats. Carbohydrates break down in the bowels yielding glucose ($C_6H_{12}O_6$). Glucose is transported to the cells, where it reacts with O_2 in a series of steps that finally produce $CO_2(g)$ and $H_2O(l)$, and the enthalpy for the overall reaction is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
$$\Delta H^\circ = -2816\ \text{kJ}$$

The accepted mean energy value or content for carbohydrates is 17 kJ/g (or 4 kcal/g).

Fats produce CO_2 and H_2O both during metabolism and combustion in a calorimetric bomb. For stearin $C_{57}H_{110}O_6$, a typical fat, the combustion reaction is as follows:

$$2C_{57}H_{110}O_6(s) + 163O_2(g) \rightarrow 114CO_2(g) + 110H_2O(l)$$
$$\Delta H^\circ = -75,520\ \text{kJ}$$

The accepted mean energy value of fats is 38 kJ/g (or 9 kcal/g). The metabolism of proteins produces less energy than in the calorimeter combustion because the products are different. In a calorimetric bomb, the nitrogen atoms of proteins are liberated as N_2; in the organism, they are liberated as urea $(NH_2)_2CO$. On average, proteins produce 17 kJ/g (or 4 kcal/g) in the organism, the same as carbohydrates.

The preceding enthalpy combustion values were obtained from enthalpy of formation data for solid glucose and stearin, and liquid water. In this computational exercise, these substances are considered in vacuum (gas phase), so enthalpy results will not be exactly the same. Although enthalpy and internal energy are distinct thermochemical concepts, ΔnRT values for the reactions with the compounds considered represents a minor contribution.

EXPERIMENTAL DETAILS

This computational exercise was developed for first year students taking chemistry. They worked in groups of three students maximum per PC. Each team worked with two food items at least. Prior to performing calculations, discussions were carried out regarding several aspects on chemistry of nutrition. The software was introduced and the calculations were carried out in two sessions of 2.5 h each.

Computational Package

Our results reported in this work were obtained using Hyperchem.6[18] package at PM3 level calculations. Some students have also performed the lab with Spartan Student,[19] and any computational package with semiempirical level calculations (e.g., MOPAC,[20] AMPAC,[21] GAUSSIAN[22]) could be used similarly.

Prelab Reading

Prior to the laboratory session, students had to read the lab manual (provided in the Supporting Information), sections of the text book addressing foods (e.g., "Foods" from section 5.8 Foods and Fuels of Brown et al.[9]), and specific up-to-date articles (e.g., "Clean Your Plate, Save Energy", Brown, V.;[23] "It's

dx.doi.org/10.1021/ed2008894 | J. Chem. Educ. XXXX, XXX, XXX−XXX

Your Food Talking", Fessenden, M.;[24] "Cranberries in your medicine cabinet", Halford, B;[25] "The New Naturals", Bomgardner, M. M.;[26] "Food Fights", Bomgardner, M. M.;[27] "A natural Green boost for muscles", Ritter, S. K., Bomgardner, M. M.[28]).

The purpose of this early activity was to introduce students in the reading of pertinent professional journals; to identify unknown terminology, and cooperatively start constructing a glossary. Each group was asked to bring at least one question referring to the assigned article to promote discussion in the groups.

Computations

The laboratory was then conducted in the following stages: The molecular structure to be analyzed was built on the PC screen. Figure 3 shows alanine, arginine, and stearin as example molecules. The molecular geometry was optimized through molecular mechanics techniques[29−33] and the energy was further minimized by application of a semiempirical method (e.g., AM1[34] or PM3[35−37]). The heat of formation of the compound was recorded, as calculated by the semiempirical method chosen above. The same procedure was followed for the combustion products, i.e., H_2O, CO_2, and $(NH_2)_2CO$, when applicable. The balanced equation for the combustion reaction of the compound under analysis was written. Figure 4 compares the visual impact of the oxidation of glucose written as a chemical equation and as seen by the students using Hyperchem.

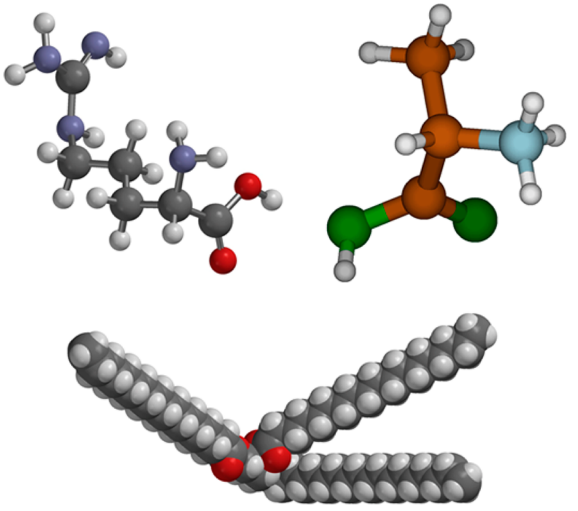


Figure 3. Example starting points of a calculation. (Top left) Molecular structure of arginine modeled with Spartan using balls and sticks. (Top right) Molecular structure of alanine prepared with GaussView[38] using Molden[39] for visualization. (Bottom) Stearin modeled with Spartan using space filling.

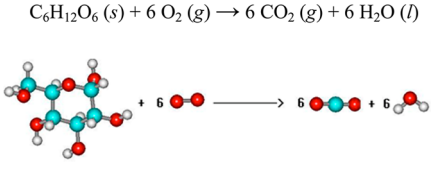


Figure 4. Oxidation of glucose to CO_2 and H_2O written, above, as a chemical equation and, below, visualized using Hyperchem.

The molar heat of combustion for that compound was calculated by means of Hess's Law, as well as the kilocalories per gram released. The results were analyzed, discussed, and compared to data from references, and conclusions were drawn. Related questions or calculations about nutrition completed the discussion.

RESULTS AND ANALYSIS

Given that only isolated molecules are modeled, all calculations are performed in the gas phase, leading to some differences between data reported in combustion equations presented above and values reported in Table 1. The values of formation and combustion heats obtained via Hyperchem with the PM3 method are reported in Table 1 for glucose, stearin, stearic acid, some amino acids and dipeptides, and combustion products. For example, to calculate the value of $\Delta_c H$ for the dipeptide formed by phenylalanine−aspartic acid, the reaction considered was

$$C_{13}H_{16}N_2O_5(g) + 13O_2(g) \rightarrow (NH_2)_2CO(g) + 12CO_2(g) + 6H_2O(g)$$

Data in Table 1 corresponding to Spartan-10, as yielded by AM1 calculations, are within a 10% difference, with the exception of glucose at 11.8%. The differences in combustion calculations via Hyperchem and Spartan in Table 1 are less than 7%, except for some dipeptides at 13% (this increased percentage may be additionally due to conformational effects, not only to the different methods used).

For this exercise, students had to know *a priori* the mass percentage composition of certain food items; they chose the degradation products for each nutrient; then they derived, with semiempirical calculations, the energy per gram released in the complete combustion of the component and they reported the total energy released by every 100 g of the food item in question (or per serving, depending on the local nutrition labels). They finally compared their values with those published on the package of the item.

In Table 2, the energy values of several common food items are shown (negative signs are omitted), obtained for a given selection of degradation products (see footnotes in Table 1).

Calories in Table 2 are thermochemical and the errors correspond to the deviation regarding values obtained according to footnote *b* in Table 2. The errors for 15 food items range from 3 to 22%, with an average error of ∼12%. The calculations performed in the lab with Spartan provide a reasonable approximation to the reported energy values. If desired, this exercise could be complemented with experimental thermochemistry determinations of any food item whose composition in fats, carbohydrates and proteins is reported on its package. Our students worked with marshmallows and peanuts, and the results as compared to the packaging information were within ∼1−20% error for computational calculations, and 60−85% error for experimental thermochemistry determinations.

An example of the discussion question posed to the students was as follows: How many kilometers can an average person run with the energy provided by 100 g (3.5 oz) of beef? According to Brown, T. L. et al.,[9] an average person uses 62 kcal/km while running. Students were able to calculate that beef provided energy for 4.42 km (2.75 mi), showing that the first-principles atomistic calculations in this lab can be used to answer everyday life questions.

dx.doi.org/10.1021/ed2008894 | J. Chem. Educ. XXXX, XXX, XXX−XXX

Table 1. Formation and Combustion Enthalpies of Some Examples of Amino Acids, Fats, Carbohydrates, Dipeptides and Combustion Products with Hyperchem 6 (HyCh) and Spartan 10[a]

Compounds	$\Delta_f H$ (kJ/mol) HyCh	$\Delta_f H$ (kJ/mol) Spartan	$\Delta_c H$ (kJ/mol) HyCh	$\Delta_c H$ (kJ/g) HyCh	$\Delta_c H$ (kJ/g) Spartan
Alanine	−419.95	−421.84	−1434.61	−16.12	−15.02
Arginine	−359.41	−338.50	−2078.93	−11.95	−12.15
Stearin	−2223.04	−2460.17	−30369.65	−34.12*	−33.89
Stearic Acid	−784.17	−862.77	−9649.53	−33.98	−33.78
Glucose	−1116.08	−1265.22	−2361.82	−13.12*	−12.37
Phenylalanine-aspartic acid	−837.89	−861.88	−4947.54	−17.67*	−17.20
Arginine-aspartic acid	−895.12	−889.34	−3210.49	−11.11	−12.60
Glycine-glutamine	−740.69	−768.10	−2257.59	−11.12	−9.65
CO_2	−355.99	−334.00			
Urea	−171.73	−188.07			
H_2O	−223.67	−247.86			

[a]Complete tables in Supporting Information. *, value used to calculate the energy content of food items.

Table 2. Energy Values for Several Food Items

Food Item	Carbohydrates, %	Fat, %	Protein, %	Energy calc. (kJ/g)[a]	Energy conv. (kJ/g)[b]	Energy calc. (kcal/g)	Energy conv. (kcal/g)	Ref. data,[c] (kJ/g)	Error, %
Beef	0	21.1	23.6	11.41	12.03	2.73	2.88	15	5
Bread	52	3	9	9.45	11.51	2.26	2.75	12	18
Cheese	0	33.5	26	16.07	17.15	3.84	4.10	20	6
Eggs	0.7	10	13	5.82	6.13	1.39	1.46	6	5

[a]Obtained using the values (*) of Table 1. [b]Obtained using the conventional values of 17 kJ/g for carbohydrates and proteins, and 38 kJ/g for fat. [c]Extracted values from usual textbooks (Brown et al;[9] Chang;[40] Atkins and Beran[41]).

CONCLUSION

This lab presents different aspects of general chemistry curriculum: stoichiometric calculations, mass composition, thermochemistry, an introduction to molecular modeling and theoretical chemistry, biochemistry, and links with real life through nutrition and the caloric content of food items.

The students can find good agreement with the calculations performed in this computational laboratory and food item data as reported on the labels. When combined with simplistic calorimetric experiments, the calculated values may be more accurate than the experimental determinations, leading to interesting discussions about the limitations of each method. The procedure described here opens the possibility of considering amino acids with sulfur, tripeptides, and other (larger) molecules to provide results for a greater range of food items.

As presented in the introduction, the instructor can propose different questions to the students to help them to find relations between this exercise and real life. Students were able to calculate the amount of a particular food item that would enable a model person to perform a particular activity, showing that the first-principles atomistic calculations in this lab can be used to answer everyday life questions.

ASSOCIATED CONTENT

Supporting Information

Expanded tables of values for enthalpies of amino acids, dipeptides and energy content of food items and the student handout. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Values obtained via AM1 in Spartan 10 were kindly provided by an anonymous reviewer and are gratefully acknowledged.

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