

ELECTRONS IN GRAPHENE AND FULLERENES

Introduction

Novel carbon structures such as graphene sheets, nanotubes and bucky-balls are generating a lot of interest in fields as diverse as hydrogen storage and electronics (see, for example, [1]). Many of their exciting properties stem from their electronic structure, and that is what this project will explore.

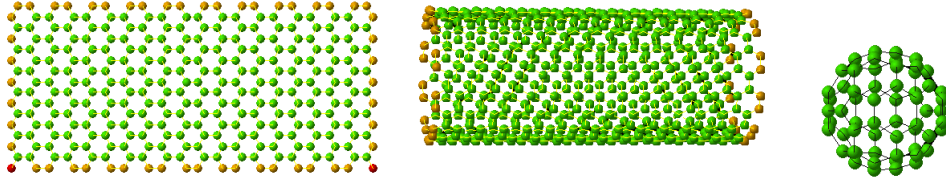


Figure 1: A sheet of graphene (left), a sheet rolled into a nanotube (centre) and a C_{60} buckyball (right): taken with modifications from [3].

The Model

In the project, we use a simplified electronic structure method called Extended Hückel Theory, in which all the messy details of electron-electron interactions are ignored. We write the wave-function for each electron in the system as a weighted sum of atomic functions,

$$\Psi = \sum_I^{(\text{atoms})} \sum_i^{(\text{functions on } I)} c_{Ii} \psi_{Ii},$$

and we express everything in terms of the overlap integrals

$$S_{IiJj} = \int \psi_{Ii} \psi_{Jj} dV,$$

and electronic energies for atoms ϵ_{Ii} . Then we build a Hamiltonian matrix

$$H_{IiIi} = \epsilon_{Ii},$$

and

$$H_{IiJj} = \frac{1}{2} \kappa S_{IiJj} (\epsilon_{Ii} + \epsilon_{Jj}),$$

and find the energies and coefficients of the wavefunctions by solving the generalised eigenvalue problem

$$Hc = ES c.$$

We shall confine ourselves to systems containing Carbon and Hydrogen, and the atomic functions will be just a $1s$ function on each Hydrogen and $2s$, $2px$, $2py$ and $2pz$ functions on each Carbon¹. The necessary formulae are given in the appendix. Note, though, that these overlaps are calculated in a coordinate system in which the z axis is along the line joining the atoms: they must be turned into a global set of coordinates by using rotation matrices. The numerical parameters which are needed are the exponents α , which are 1.625 Bohr^{-1} for Carbon and 1.200 Bohr^{-1} for Hydrogen ($1 \text{ Bohr} = 0.529177 \text{ \AA}$), and the energies ϵ are -0.7144 Hartree for Carbon s , -0.3921 Hartree for Carbon p , -0.5000 Hartree for Hydrogen ($1 \text{ Hartree} = 13.69 \text{ eV}$). The parameter κ is taken to be 1.75.

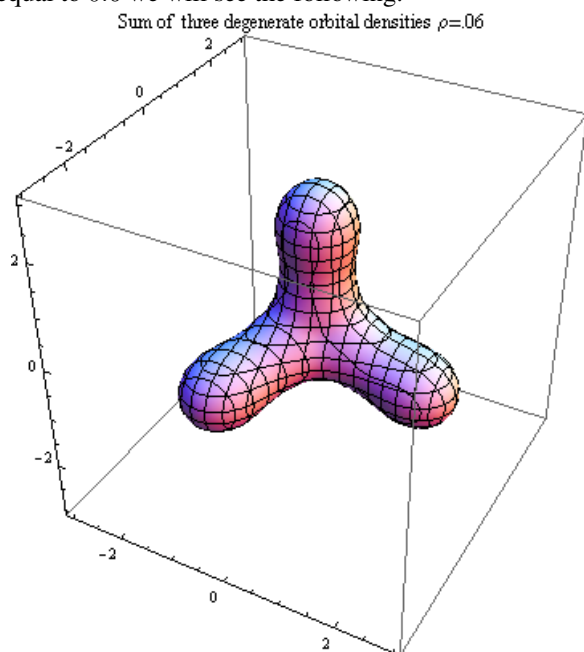
¹In the quantum mechanics and atomic & molecular physics courses you will have used p functions which are represented by complex spherical harmonics rather than the real functions we use here.

Example

As a simple starting case, consider the Methane molecule. The geometry, in Angstroms, is

Atom	x	y	z
C	0	0	0
H	0	0	1.1
H	1.03709	0	-0.366667
H	-0.518545	0.898146	-0.366667
H	-0.518545	-0.898146	-0.366667

so we have 4 atoms and $4 + 1 + 1 + 1 + 1 = 8$ atomic functions in the problem. When we set up the eigenproblem we will get 8 energies and 8 corresponding functions. We have 8 valence electrons to accommodate, but each function can contain two electrons, one with spin up and one with spin down. We should find, then, that we have to occupy four functions, one with energy E_1 and three degenerate ones with energy $E_2 = E_3 = E_4$. If we use ContourPlot3D to show the surface at which the total electron density from the three functions (i.e. $\Psi_2^2 + \Psi_3^2 + \Psi_4^2$) is equal to 0.6 we will see the following.



The Project

The aim of the project is to set up a program to carry out EHT calculations. To do this efficiently will need careful consideration of an appropriate data structure – without this each problem is going to need messy programming to set up the matrices for the eigenvalue problem. You should test your code on methane.

Then apply the code to a selection of graphene sheets, nanotubes etc. There are various sites on the web which will help with constructing geometries for nanotubes (for example, <http://k.lasphost.com/tubeasp/tubea>) and geometries for various fullerenes are also available on the web. One interesting question is how big the difference in energy is between the highest occupied orbital (HOMO) and the lowest unoccupied one (LUMO): if this is very small the system is probably metallic, whereas if it is large the system is an insulator or a semiconductor.

References

- [1] http://www.solid-state.com/display_article/331055/5/none/none/Feat/Graphene:-a-playground-for-physics
- [2] R. Hoffmann An Extended Hckel Theory. I. Hydrocarbons. *J. Chem. Phys* **39**, 1397-1412 (1963)
- [3] <http://reizei.t.u-tokyo.ac.jp/~maruyama/agallery/agallery.html>
- [4] M. Wolfsberg and L. J. Helmholz *Journal of Chemical Physics* **20**, 837 (1952)
- [5] R. Hoffmann and W. N. Lipscomb *Journal of Chemical Physics* **36**, 2179 (1962); **37**, 2872 (1962)

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Appendix

The normalised forms of the wavefuctions are as follows,

$$\begin{aligned}\psi_{1s} &= \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r) \\ \psi_{2s} &= \sqrt{\frac{\alpha^5}{(3\pi)}} r \exp(-\alpha r) \\ \psi_{2px} &= \sqrt{\frac{\alpha^5}{\pi}} x \exp(-\alpha r)\end{aligned}$$

with the forms of the $2py$ and $2pz$ functions being similar to $2px$.

Here are the overlap integrals, first for cases where the exponents are not equal (k is the ratio of exponents, and

$t = \alpha_1 R$ where α_1 is the exponent of the first function and R is the separation.

$$\begin{aligned}
S(1s, 1s) &= (8k((-4k + k(-1 + k^2)t) \exp(-t) \\
&\quad + (4k + (-1 + k^2)t) \exp(-kt))\sqrt{k}/((-1 + k^2)^3 t) \\
S(2s, 1s) &= (8k^2((-4 - 20k^2 + (-1 + k^2)(1 + 3k^2)t) \exp(-t) \\
&\quad + (4 + 20k^2 + 8k(-1 + k^2)t + (-1 + k^2)^2 t^2) \exp(-kt))\sqrt{k}/(\sqrt{3}(-1 + k^2)^4 t) \\
S(2pz, 1s) &= (8k^2((-24k - 24kt + 4k(-1 + k^2)t^2) \exp(-t) \\
&\quad + (24k + 24k^2 t + 8k(-1 + k^2)t^2 + (-1 + k^2)^2 t^3) \exp(-kt))\sqrt{k}/((-1 + k^2)^4 t^2) \\
S(2s, 2s) &= (8k^2((20 + 152k^2 + 20k^4 - 8(-1 + k^2)(1 + 5k^2)t + (-1 + k^2)^2(1 + 3k^2)t^2) \exp(-t) \\
&\quad + (-20 - 152k^2 - 20k^4 - 8k(-1 + k^2)(5 + k^2)t \\
&\quad - (-1 + k^2)^2(3 + k^2)t^2) \exp(-kt))\sqrt{k}/(3(-1 + k^2)^5 t) \\
S(2pz, 2s) &= (-8k^2((-168k - 24k^3 - 24k(7 + k^2)t \\
&\quad + 4k(-1 + k^2)(11 + k^2)t^2 - 4k(-1 + k^2)^2 t^3) \exp(-t) \\
&\quad + (168k + 24k^3 + 24k^2(7 + k^2)t + 8k(-1 + k^2)(5 + k^2)t^2 \\
&\quad + (-1 + k^2)^2(3 + k^2)t^3) \exp(-kt))\sqrt{k}/(\sqrt{3}(-1 + k^2)^5 t^2) \\
S(2pz, 2pz) &= (-32k^2((96k + 96kt + 48kt^2 - k(-1 + k^2)(11 + k^2)t^3 + k(-1 + k^2)^2 t^4) \exp(-t) \\
&\quad + (-96k - 96k^2 t - 48k^3 t^2 - (-1 + k^2)(1 + 11k^2)t^3 \\
&\quad - k(-1 + k^2)^2 t^4) \exp(-kt))\sqrt{k}/((-1 + k^2)^5 t^3) \\
S(2px, 2px) &= (32k^2((48k + 48kt - 12k(-1 + k^2)t^2 + k(-1 + k^2)^2 t^3) \exp(-t) \\
&\quad + (-48k - 48k^2 t - 12k(-1 + k^2)t^2 - (-1 + k^2)^2 t^3) \exp(-kt))\sqrt{k}/((-1 + k^2)^5 t^3)
\end{aligned}$$

and the forms for equal exponents are rather simpler:

$$\begin{aligned}
S(1s, 1s) &= ((3 + 3t + t^2) \exp(-t))/3 \\
S(2s, 1s) &= ((9 + 9t + 4t^2 + t^3) \exp(-t))/(6\sqrt{3}) \\
S(2pz, 1s) &= (t(3 + 3t + t^2) \exp(-t))/6 \\
S(2s, 2s) &= ((45 + 45t + 20t^2 + 5t^3 + t^4) \exp(-t))/45 \\
S(2pz, 2s) &= (t(15 + 15t + 7t^2 + 2t^3) \exp(-t))/(30\sqrt{3}) \\
S(2pz, 2pz) &= ((15t + 15t^2 + 3t^3 - 2t^4 - t^5) \exp(-t))/(15t) \\
S(2px, 2px) &= ((15t + 15t^2 + 6t^3 + t^4) \exp(-t))/(15t)
\end{aligned}$$

It may be helpful, when checking your code, to know that the Hamiltonian matrix for the methane molecule for the geometry given is

$$\begin{pmatrix}
-0.7144 & 0. & 0. & 0. & -0.46937 & -0.46937 & -0.46937 & -0.46937 \\
0. & -0.3921 & 0. & 0. & 0. & -0.39467 & 0.197335 & 0.197335 \\
0. & 0. & -0.3921 & 0. & 0. & 0. & -0.341794 & 0.341794 \\
0. & 0. & 0. & -0.3921 & -0.418611 & 0.139537 & 0.139537 & 0.139537 \\
-0.46937 & 0. & 0. & -0.418611 & -0.5 & -0.157918 & -0.157918 & -0.157918 \\
-0.46937 & -0.39467 & 0. & 0.139537 & -0.157918 & -0.5 & -0.157918 & -0.157918 \\
-0.46937 & 0.197335 & -0.341794 & 0.139537 & -0.157918 & -0.157918 & -0.5 & -0.157918 \\
-0.46937 & 0.197335 & 0.341794 & 0.139537 & -0.157918 & -0.157918 & -0.157918 & -0.5
\end{pmatrix}$$