

Quantum Calculations in CHEM 870

Approximations to Solve Schrödinger:
Introduction & Background

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Outline

1 Foundations

- Motivation
- The He Atom
- Slater orbitals and determinants

2 Self-Consistent Procedure

- Hartree-Fock
- Electron Correlation
- Introduction to basis sets

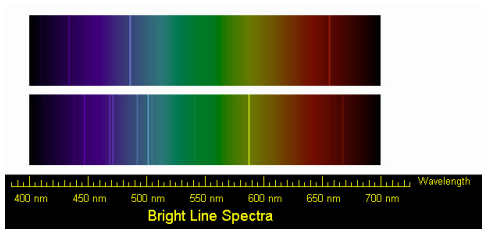
3 The Secular Equation

Electronic Structure and Quantum Properties

Why do we care?

Spectroscopy is how we identify atoms and molecules.

"The skepticism over the possibility of an element existing in space but not on Earth is perhaps no surprise (in 1868), given that it was the first of its kind."



The He Atom

The Schrödinger Equation for He

The goal is to solve for E and ψ :

$$\left[\hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \quad (1)$$

The Hamiltonian Operator for He

using atomic units

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (2)$$

What's \hat{H}_H in atomic units?

The Variational Method

Start with a trial wavefunction. For example, $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$.

The 1s type wavefunction

$$\psi_{1s}(\mathbf{r}) = \frac{\zeta^3}{\pi} e^{-\zeta(r)} \quad (3)$$

Multiply two of these to get the trial ψ for He. You write it:

The Eigenvalue, E

$$E(\zeta) = \zeta^2 - \frac{27}{8}\zeta \quad (4)$$

$$E_{min} = -2.84766E_h \quad (5)$$

Compare to the experimental value of $-2.9033E_h$

The Variational Method *can* work well

The ionization energy is wrong by 150 kJ/mol, the energy in a chemical bond!

Ionization energy

$$IE = E_{He^+} - E_{He} \quad (6)$$

$$IE = -2 + 2.8477 = 0.8477 E_h \quad (7)$$

Compare to the experimental value of $0.9033 E_h$.

To improve, we can update the trial wavefunction.

- 1 Use a linear combination of 1s orbitals with two different values of ζ
- 2 Use a linear combination of a '1s' and '2s' orbital
- 3 Use a linear combination of many orbitals - Slater

The Variational Method with Slater orbitals

In the 1930s, John Slater introduced simplified orbitals to replace hydrogenic type orbitals.

Slater orbitals

$$S_{nlm_l}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^{m_l}(\theta, \phi) \quad (8)$$

N_{nl} is a normalization constant and depends on ζ , while $Y_l^{m_l}$ are the spherical harmonics.

More accurate energies using linear combinations of Slater type orbitals are $E = -2.8617E_h$ with $IE = 0.8617E_h$.

This *Variational* value is better (lower) than the product of two hydrogen 1s orbitals and gives $E = -2.8477E_h$. The lowest possible E is called the *Hartree-Fock limit*.

Example 1s orbital (double zeta) for helium:

$$\phi_{1s}(r) = 0.843785 S_{1s}(\zeta = 1.45363) + 0.180687 S_{1s}(\zeta = 2.91093) \quad (9)$$

Improvements to linear combinations of 'orbitals'

If time is of no concern, many calculations can be done to improve computation:

Hylleraas includes interelectronic distance, r_{12}

$$\psi(\mathbf{r}_1, \mathbf{r}_2, r_{12}) = e^{\zeta r_1} e^{\zeta r_2} (1 + cr_{12}) \quad (10)$$

where ζ and c are the variational parameters to give $E = -2.8913E_h$

Pekeris included 1078 parameters to give $E = -2.903724375E_h$ – very close to experiment!

Slater determinants are antisymmetric wtr e^- exchange

Spin orbitals contain a spatial and spin function

$$\Psi(x, y, z, \sigma) = \psi(x, y, z)\alpha(\sigma) \quad (11)$$

or for the other spin, $\beta(\sigma)$.

Slater's determinantal wave function

Consider a two electron wavefunction for He,

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \quad (12)$$

which is antisymmetric upon exchanging rows or columns.

The determinant also ensures that two electrons cannot be placed into the same orbital. It can be extended to an N electron system, using various spatial orbitals.

Goal: write a separate Hamiltonian for each electron

The Hartree-Fock wavefunction is product of 1 e^- wavefunctions

For a Helium atom

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \quad (13)$$

and the probability distribution of electron i is $\psi^*(\mathbf{r}_i)\psi(\mathbf{r}_i)d\mathbf{r}_i$.

The potential energy that electron 1 experiences from electron 2 is

$$V_1^{\text{eff}}(\mathbf{r}_1) = \int \psi^*(\mathbf{r}_i) \frac{1}{r_{12}} \psi(\mathbf{r}_i) d\mathbf{r}_i \quad (14)$$

which is the effective potential from electron 2's charge density.

Now we can define a Hamiltonian operator for each electron.

The Hartree-Fock equation and the effective one electron operator

The effective one-electron Hamiltonian is

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{\text{eff}}(\mathbf{r}_1) \quad (15)$$

recalling $V_1^{\text{eff}}(\mathbf{r}_1) = \int \psi^*(\mathbf{r}_i) \frac{1}{r_{12}} \psi(\mathbf{r}_i) d\mathbf{r}_i$

The Schrödinger equation for the effective Hamiltonian

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1)\psi^*(\mathbf{r}_1) = \varepsilon_1\psi(\mathbf{r}_1) \quad (16)$$

is called the *Hartree-Fock* equation.

There is an equivalent equation for the electron 2! This formalism extends to systems with N electrons, with V^{eff} updated.

The Self-Consistent Procedure is required because of V^{eff}

To solve for the energy, E :

$$E = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1) \psi^*(\mathbf{r}_2) \hat{H} \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \quad (17)$$

$$E = I_1 + I_2 + J_{11} \quad (18)$$

$$I_j = \int d\mathbf{r}_j \psi^*(\mathbf{r}_j) \left(-\frac{1}{2} \nabla_j^2 - \frac{Z}{r_j} \right) \psi(\mathbf{r}_j) \quad (19)$$

$$J_{11} = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1) \psi(\mathbf{r}_1) \frac{1}{r_{12}} \psi(\mathbf{r}_2)^* \psi(\mathbf{r}_2) \quad (20)$$

where J_{11} is the Coulomb integral.

This equation must be solved by a self-consistent field method because $V_1^{\text{eff}}(\mathbf{r}_1)$ depends on $\psi(\mathbf{r}_2)$, which is what we are solving for (see McQuarrie 9.3).

The Self-Consistent Procedure gives Hartree-Fock orbitals

To solve for the orbitals:

Guess: $\Psi(r)$

Evaluate: $V_1^{\text{eff}}(r_1)$

Consistent? $\Psi(r)$ vs. $\Psi(r_1)$

Solve for: $\Psi(r_1)$

The eigenvalue, ε_1 , gives the –ionization energy.

$$\varepsilon_1 = \int d\mathbf{r}_1 \psi^*(\mathbf{r}_1) \hat{H}_1^{\text{eff}} \psi(\mathbf{r}_1) \quad (21)$$

$$\varepsilon_1 = h_1 + J_{11} \quad (22)$$

$$\varepsilon_1 = E - I_2 \quad (23)$$

Get the Self-Consistent Field (SCF) using Computers

We are going to use the ORCA software to calculate the SCF of H_2 molecules.

This software is available on NanoHub, so first you have to sign up for an account! Go to nanohub.org

Follow my Tutorial 1 handout and guiding slides.

Hartree-Fock equations are missing Correlation between electrons!

For the Helium atom

$$E \neq \varepsilon_1 + \varepsilon_2 = (I_1 + J_{11}) + (I_2 + J_{11}) \quad (24)$$

$$E_{\text{exact}} = -2.9037E_h \quad (25)$$

$$\text{correlation energy} = E_{\text{corr}} \quad (26)$$

$$= E_{\text{exact}} - E_{\text{HF}} \quad (27)$$

$$= (-2.9037 + 2.8617) = -0.420E_h \quad (28)$$

E_{corr} for the helium atom is roughly the same magnitude of a chemical bond - 110 kJ/mol. A similar discrepancy is found using the Variational method with 1s type wavefunctions.

Calculating Correlation and Ionization Energies

Now let's use computational chemistry to solve for the He atom's energy!

We'll see how we can improve the ionization energy by changing the basis set in Tutorial 2

The next slides will introduce basis sets, but a more thorough explanation and testing will occur later in the semester.

Introduction to Basis Sets - More is Better!

Recall that a linear combination of Slater orbitals (S_n) is better than using a simple product of 1s type wavefunctions (or a determinant).

Using different values for ζ also improves accuracy: double or triple zeta.

Comparing the 1s orbital vs. double zeta for helium:

$$\phi_{1s}(r) = c_{11} S_{1s}(\zeta_1) + c_{12} S_{1s}(\zeta_2) \quad (29)$$

$$\psi_{1s}(r) = \frac{\zeta^3}{\pi} e^{-\zeta(r)} \quad (30)$$

$$\Psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) \quad (31)$$

The SVP basis set, **S**plit **V**alence **P**olarized, is the default in Tutorial 1.

SVP - linear combination of orbitals

$$\psi_n = c_1 \phi_{1s} + c_2 \phi_{2s} + c_3 \phi_{p_x} + c_4 \phi_{p_y} + c_5 \phi_{p_z} \quad (32)$$

Introduction to Basis Sets - Excited States

SVP - linear combination of orbitals

$$\psi_n = c_1 \phi_{1s} + c_2 \phi_{2s} + c_3 \phi_{p_x} + c_4 \phi_{p_y} + c_5 \phi_{p_z}$$

The functions making up the basis set $\{\phi_i\}$ are summed in a linear combinations to form the ground state, ψ_0 , and excited states, ψ_1, ψ_2, \dots

In ORCA, ψ_n coefficients are given in a table:

<i>Level</i>		0	1	2	3	4
<i>Energy</i>		-0.91	1.40	1.99	1.99	1.99
<i>OCC.</i>		2.0	0	0	0	0
0He	1s	0.59	-1.15	-0.0	0.0	0.0
0He	2s	0.51	1.19	0.0	-0.0	-0.0
0He	1pz	0.0	0.0	-0.08	-0.99	-0.12
...

Remembering Molecular Orbitals (MO)

The simplest way to make MOs for H₂ is to make a bonding and antibonding linear combination of 1s orbital on each hydrogen (1 and 2).

Bonding and Antibonding Orbitals

$$\Psi_{\text{bonding}} = \psi_{1s}(1) + \psi_{1s}(2)$$

$$\Psi_{\text{antibonding}} = \psi_{1s}(1) - \psi_{1s}(2)$$

These orbitals are *okay* for predicting the occupation of the HOMO and LUMO and spin, but do a terrible job modeling bond stretching and breaking, as we will see later.

A good exercise: draw a diagram of the MOs for O₂ using only the 1s, 2s, and 2p atomic orbitals. Show that the molecule is paramagnetic.

In contrast to MO theory, valence bond theory can also be used to predict the electronic structure and bond information. Hückel Theory is a common example taught in computational and quantum classes, which we might cover if time allows.

The Secular Equation must be solved

The Secular Equation is solved to find the energy and coefficients (a_i) that define the wavefunctions for a given basis set. It often takes the form of a determinant, both in Hückel Theory and Hartree-Fock methods.

The Hamiltonian in terms of an orthonormal Basis Set $\{\psi_i\}$

From Cramer's notation, $\Phi = \sum_i a_i \psi_i$

$$\begin{aligned}\int \Phi H \Phi d\mathbf{r} &= \int \left(\sum_i a_i \psi_i \right) H \left(\sum_j a_j \psi_j \right) d\mathbf{r} \\ &= \sum_{ij} a_i a_j \int \psi_i H \psi_j d\mathbf{r} \\ &= \sum_i a_i^2 E_i\end{aligned}$$

Because the basis set has orthonormal basis functions.

Now we need to consider bonding and overlap between atoms' $\Phi!$

The Secular Equation must be solved

There are many molecular orbitals: $\{\Phi_j\}$.

If the basis set consists of functions centered on different atoms, they are no-longer orthogonal - they may have overlap!

To find energy, recall basis set is not orthogonal.

$$\begin{aligned} E &= \frac{\int (\sum_i a_i \psi_i) H (\sum_j a_j \psi_j) d\mathbf{r}}{\int (\sum_i a_i \psi_i) (\sum_j a_j \psi_j) d\mathbf{r}} \\ &= \frac{\sum_{ij} a_i a_j \int \psi_i H \psi_j d\mathbf{r}}{\sum_{ij} a_i a_j \int \psi_i \psi_j d\mathbf{r}} \\ &= \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}} \end{aligned}$$

where H_{ij} is called the *resonance integral* and S_{ij} is the *overlap integral*.

We want to choose $\{a_i\}$ to minimize the energy, E_j of each orbital, Φ_j .

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The Secular Equation: step 1) $\frac{\partial E}{\partial a_k} = 0, \forall k$

You could minimize the energy by taking the derivative for each j if there were only a couple ψ_j in your basis set...

To find energy, find the best coefficients, a_i :

$$E \sum_{ij} a_i a_j S_{ij} = \sum_{ij} a_i a_j H_{ij} \psi_j$$

$$\sum_i a_i (H_{ki} - ES_{ki}) = 0, \forall k$$

where the second equation comes from $\frac{\partial E}{\partial a_k} = 0$.

The size of your basis set (the number of $\{\psi_i\}$) determines how many equations need to be solved. We don't want $a_i = 0$, so $(H_{ki} - ES_{ki}) = 0$ for each i in the sum. It's hard to solve for a_i and E by hand...

Linear algebra to the rescue!

The Secular Equation: step 2) use a determinant

Taking the derivative wrt $a_k \forall k$ gives a set of N equations and involves N unknowns (the a_k). Linear algebra shows us that the non-trivial solution is found *if and only if* the determinant given below = 0.

This Determinant is called **The Secular Equation**

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2N} - ES_{2N} \\ \dots & \dots & \dots & \dots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \dots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (33)$$

Recall, H_{ij} and S_{ij} are integrals, set by the structure/bonding of the molecule. Thus, we need to solve for E !

In general, there will be N roots from solving N linear equations: N values of E_j that satisfy the secular equation. Some values of E_j may be degenerate.

Each value of E_j is associated with a set of coefficients, a_{ij} , to give Φ_j

Update the Hartree-Fock Hamiltonian - exchange

Hartree-Fock is always missing correlation energy. Unless antisymmetric wavefunctions are used (*wrt* exchange of electrons), we are also missing exchange energy.

The Coulomb & exchange integrals for He's Slater Determinant

$$\begin{aligned}\Psi(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1))\end{aligned}$$

$$E = \langle \Psi(1,2) | \hat{H} | \Psi(1,2) \rangle$$

$$E = I_1 + I_2 + 2J_{11} - K_{11}$$

$$J_{11} = \langle 1s\alpha(1)1s\beta(2) | \frac{1}{r_{12}} | 1s\alpha(1)1s\beta(2) \rangle$$

$$K_{11} = \langle 1s\alpha(1)1s\beta(2) | \frac{1}{r_{12}} | 1s\alpha(2)1s\beta(1) \rangle$$

The Secular Equation and Hartree-Fock

The Fock operator

Back to Cramer's notation: Φ_j is an orbital and $\{\psi_i\}$ are the basis set.

$$\hat{F}(r_1)\Phi_j(r_1) = \varepsilon_j\Phi_j(r_1) \quad (34)$$

$$\hat{F}(r_1)\Phi_j(r_1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} + \sum_i^N [2\hat{J}_i(r_1) - \hat{K}_i(r_1)] \quad (35)$$

$$F_{\mu\nu} = \langle \psi_\mu(r_1) | \hat{F}(r_1) | \psi_\nu(r_1) \rangle, \Phi_j = \sum_i^N a_i \psi_i \quad (36)$$

$$0 = \begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \dots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \dots & F_{2N} - ES_{2N} \\ \dots & \dots & \dots & \dots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \dots & F_{NN} - ES_{NN} \end{vmatrix} \quad (37)$$

The Secular Equation and Hartree-Fock

We need to keep track of our indices:

μ and ν are indices for the N basis function. i and j index molecular orbitals (electrons) and A tracks the nuclei.

The computer will solve this determinant to get ε_j

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \dots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \dots & F_{2N} - ES_{2N} \\ \dots & \dots & \dots & \dots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \dots & F_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (38)$$

where

$$F_{\mu\nu} = \langle \mu | -\frac{1}{2}\nabla^2 | \nu \rangle - \sum_A \langle \mu | \frac{1}{r_{jA}} | \nu \rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma)],$$

$$(\mu\nu | \lambda\sigma) = \int \int \psi_\mu(1)\psi_\nu(1)\frac{1}{r_{12}}\psi_\lambda(2)\psi_\sigma(2)d\mathbf{r}(1)d\mathbf{r}(2), \text{ and}$$

$$P_{\lambda\sigma} = 2 \sum_i a_{\lambda i} a_{\sigma i} \text{ for all occupied orbitals; } P_{\lambda\sigma} = \text{the density matrix.}$$

The quantum chemistry software solves all the integrals - lucky!

The number of integrals in the Secular Determinant

Best explanation from Lewars page 236:

Consider a basis set of $N = 7$ basis functions (for example in a small molecule like HHe^+ .)

Around N^4 integrals are needed

Start count by noting the 7×7 matrix = 49 terms.

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \dots & F_{17} - ES_{17} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \dots & F_{27} - ES_{27} \\ \dots & \dots & \dots & \dots \\ F_{71} - ES_{71} & F_{72} - ES_{72} & \dots & F_{77} - ES_{77} \end{vmatrix} = 0$$

The Coulomb and exchange integrals, $\sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)]$, account for at least $2 * 49 = 98$ terms (sum over all pairs of basis functions) in each determinant element.

But there are many duplicates, so the estimate of the number of integrals to solve is estimated as $N^4/8$.

The Secular Equation gives the molecular orbital energies

Go back and look at your output from solving for H₂ using Hartree-Fock. Check to see that the number of basis functions used gives the same number of molecular orbital energies!

The computer will solve this determinant to get ϵ_j

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \dots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \dots & F_{2N} - ES_{2N} \\ \dots & \dots & \dots & \dots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \dots & F_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (39)$$

where

$$F_{\mu\nu} = \langle \mu | -\frac{1}{2}\nabla^2 | \nu \rangle - \sum_A \langle \mu | \frac{1}{r_{jA}} | \nu \rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma)],$$

$$(\mu\nu | \lambda\sigma) = \int \int \psi_\mu(1)\psi_\nu(1)\frac{1}{r_{12}}\psi_\lambda(2)\psi_\sigma(2)d\mathbf{r}(1)d\mathbf{r}(2), \text{ and}$$

$$P_{\lambda\sigma} = 2 \sum_i a_{\lambda i} a_{\sigma i} \text{ for all occupied orbitals; } P_{\lambda\sigma} = \text{the density matrix.}$$

The density matrix gives us electron density!

The Secular Equation is solved during the SCF procedure

Cramer's SCF flow chart:

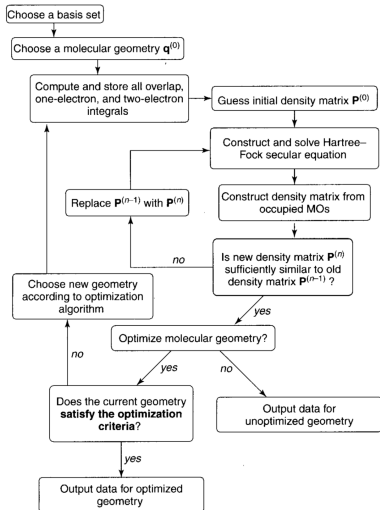


Figure 4.3 Flow chart of the HF SCF procedure. Note that data for an unoptimized geometry is referred to as deriving from a so-called 'single-point calculation'

Pick the form of the Helium atom Hamiltonian that is not correct

(a)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

(b)

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

(c)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$