Ground state energy of quantum dots using the coupled cluster method

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Something about coupled-cluster... Preferably doubles.

CONTENTS

I. INTRODUCTION

In this project we will study the ground state energy of quantum dots.

II. THEORY

In this project we will study a system of N interacting electrons. We will be looking at a Hamiltonian consisting of a one-body and a two-body part. The one-body part is given by

$$h(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2\mathbf{r}_i^2, \qquad (1)$$

where we use natural units $\hbar = c = e = 1$ and set the mass to unity. The two-body part is the Coulomb interaction potential.

$$v(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}. \qquad (2)$$

We thus get the total Hamiltonian

$$H = h + W = \sum_{i=1}^N h(\mathbf{r}_i) + \sum_{i<j}^N v(\mathbf{r}_i, \mathbf{r}_j), \qquad (3)$$

where h is the full one-body operator and W the full two-body operator, i.e., over the entire system. Working in a

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* Project code: https://github.com/Schoyen/FYS4411

basis of L single particle functions, $\{|p\rangle\}_{p=1}^L$. We define the reference Slater determinant as

$$|\Phi_0\rangle \equiv |1, 2, \ldots, N\rangle, \qquad (4)$$

i.e., a tensorproduct of the N first single particle functions, $|i\rangle$, of the system. We call these single particle functions *occupied* as they are contained in the Slater determinant. We will denote the occupied indices with $i, j, k, l, \cdots \in \{1, \ldots, N\}$, the *virtual* states with $a, b, c, d, \cdots \in \{N+1, \ldots, L\}$ and general indices with $p, q, r, s, \cdots \in \{1, \ldots, L\}$. In terms of sets of basis functions we can write this as

$$\{|p\rangle\}_{p=1}^L = \{|i\rangle\}_{i=1}^N \cup \{|a\rangle\}_{a=N+1}^L, \qquad (5)$$

i.e., the general indexed states consists of both occupied and virtual states. Note that the single particle functions are orthonormal, i.e.,

$$\langle p|q\rangle = \delta_{pq}. \qquad (6)$$

We can construct other Slater determinants in this basis by exciting or de-exciting the reference determinant. A general excitation is labeled $|\Phi_{ij\ldots}^{ab\cdots}\rangle$ which means that we have removed the single particle functions with indices $i, j, \ldots$ from the reference and added $a, b, \ldots$. Note that

$$\langle \Phi_{ij\ldots}^{ab\cdots}|\Phi_0\rangle = 0, \qquad (7)$$

for any excitation.

A. Second quantization

Employing the creation operators, $a_p^\dagger$, and the destruction operators, a_p, we can write the Hamiltonian as

$$H = \sum_{pq} h_q^p a_p^\dagger a_q + \sum_{pqrs} w_{rs}^{pq} a_p^\dagger a_q^\dagger a_s a_r, \qquad (8)$$

where the sums are general indices over all L basis states and the matrix elements are defined as

$$h_q^p \equiv \langle p|h|q\rangle, \qquad (9)$$
$$w_{rs}^{pq} \equiv \langle pq|v|rs\rangle. \qquad (10)$$

Note that the two-body matrix elements are not antisymmetric yet.

B. The coupled cluster approximation

We approximate the true wavefunction, $|\Psi\rangle$, of the system by the coupled cluster wavefunction, $|\Psi_{CC}\rangle$, defined by

$$|\Psi_{CC}\rangle \equiv e^{T}|\Phi_0\rangle = \left(\sum_{i=0}^{n}\frac{1}{n!}T^n\right)|\Phi_0\rangle, \quad (11)$$

where the *cluster operator*, T, is given by a sum of p-excitation operators labeled T_p. They consist of *cluster amplitudes*, $t_{i\cdots}^{a\cdots}$, and creation and annihilation operators.

$$T = T_1 + T_2 + \cdots + T_p \quad (12)$$

$$= \sum_{ia} t_i^a a_a^\dagger a_i + \left(\frac{1}{2!}\right)^2 \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j + \ldots. \quad (13)$$

In the doubles approximation we limit the cluster operator to

$$T \equiv T_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \quad (14)$$

The first part of the coupled cluster method consists of constructing the cluster amplitudes using the *amplitude equations*. After we have found the amplitudes we can compute the energy.

C. Energy of the coupled cluster approximation

When we're going to compute the energy of a system using the coupled cluster approximation we would ideally want to find the expectation value of the energy using the coupled cluster wavefunction.

$$E_{CC} = \langle\Psi_{CC}|H|\Psi_{CC}\rangle. \quad (15)$$

As it turns out, this is an uncomfortable way of finding the energy as $T \neq T^\dagger$. Instead we will define what we call the *similarity transformed Hamiltonian*. We plug the coupled cluster wavefunction into the Schrödinger equation.

$$H|\Psi_{CC}\rangle = E_{CC}|\Psi_{CC}\rangle. \quad (16)$$

Next, we left multiply with the inverse of the cluster expansion, i.e.,

$$e^{-T}H|\Psi_{CC}\rangle = e^{-T}E_{CC}|\Psi_{CC}\rangle = E_{CC}|\Phi_0\rangle. \quad (17)$$

Projecting this equation on the reference state we get

$$E_{CC} = \langle\Phi_0|e^{-T}H|\Psi_{CC}\rangle = \langle\Phi_0|e^{-T}He^{T}|\Phi_0\rangle, \quad (18)$$

where in the latter inner-product we have located the similarity transformed Hamiltonian defined by

$$\bar{H} \equiv e^{-T}He^{T}. \quad (19)$$

To simplify the energy equation and the amplitude equations we use the normal ordered Hamiltonian.

$$H = H_N + \langle\Phi_0|H|\Phi_0\rangle. \quad (20)$$

The energy equation thus becomes

$$E_{CC} = \langle\Phi_0|\bar{H}|\Phi_0\rangle = E_{ref} + \langle\Phi_0|e^{-T}H_N e^{T}|\Phi_0\rangle, \quad (21)$$

where the reference energy is given by

$$E_{ref} = \langle\Phi_0|H|\Phi_0\rangle. \quad (22)$$

We now define the normal ordered similiarity transformed Hamiltonian as

$$\bar{H}_N \equiv e^{-T}H_N e^{T}. \quad (23)$$

By expanding the exponentials of this Hamiltonian and recognizing the commutators we get the Baker-Campbell-Hausdorff expansion.

$$\bar{H}_N = H_N + [H_N, T] + \frac{1}{2!}\left[[H_N, T], T\right] + \ldots. \quad (24)$$

From the connected cluster theorem we know that the only nonzero terms in the Baker-Campbell-Hausdorff expansion will be the terms where the normal ordered Hamiltonian has at least one contraction[1] with every cluster operator on its right. This lets us write the expansion as

$$\bar{H}_N = H_N + (H_N T)_c + \frac{1}{2!}\left(H_N T^2\right)_c + \ldots, \quad (25)$$

where the subscript c signifies that only contributions where at least one contraction between H_N and T has been performed will be included.

1. Coupled cluster doubles energy equation

Using the doubles approximation with the cluster operator T_2 defined in Equation 14 the energy equation becomes

$$E_{CCD} = E_{ref} + \langle\Phi_0|e^{-T_2}H_N e^{T_2}|\Phi_0\rangle. \quad (26)$$

As the doubles cluster operator doubly excites the reference and using the expansion in Equation 25 we see that we can write the energy equation as

$$E_{CCD} = E_{ref} + \langle\Phi_0|H_N(1 + T_2)|\Phi_0\rangle, \quad (27)$$

as the Hamiltonian is only able to de-excite one pair of single particle functions.

[1] T. D. Crawford and H. F. Schaefer, Reviews in Computational Chemistry, Volume 14 , 33 (2007).

Appendix A: The normal ordered Hamiltonian

When constructing the normal ordered Hamiltonian we use Wick's theorem to write the one-body, h, and the two-body, W, operators onto a normal ordered form. Specifically we define the normal ordered form in terms of Fermi vacuum. That is, an operator on normal ordered form destroys the reference Slater determinant.

$$h = \sum_{pq} h_q^p a_p^\dagger a_q = \sum_{pq} h_q^p \left(\{a_p^\dagger a_q\} + \{\overline{a_p^\dagger a_q}\} \right) \quad \text{(A1)}$$

$$= \sum_{pq} h_q^p \{a_p^\dagger a_q\} + \sum_{pq} h_q^p \delta_{p \in i} \delta_{pq} \quad \text{(A2)}$$

$$= h_N + \sum_i h_i^i, \quad \text{(A3)}$$

where we have used $\delta_{p \in i}$ to mean that p must be an occupied index. [1]

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[1] In the Wick's theorem sense.