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Exploring a system of coupled quartic oscillators with coupled cluster methods

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Many systems in physics can be modeled by harmonic oscillators. For instance, a mass attached to a spring will oscillate in a way which is well described by this model as long as the amplitude of vibration is small. For larger amplitudes the vibration becomes anharmonic as the restoring force of the spring become non-linear with respect to the displacement of the mass.
This project explores the analogue *quantum mechanical* system consisting of a system of interacting particles subjected to forces which give rise to anharmonic oscillatory motion of the particles.

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Introduction

- Quantum mechanical oscillations of a many-body system about a local potential minimum can in a first approximation be modeled by a set of harmonic oscillators about a local potential minimum. In this approximation the interaction potential of the system only retaining the lowest non-zero term in a Taylor expansion of the potential energy of the system around an equilibrium point, i.e. the term

$$\sum_{rs}\left(\frac{\partial^2 V}{\partial x_r x_s}\right)_{eq} x_r x_s$$

- The motion decouples into a system of independent quantum oscillators which can be compactly expressed in terms of bosonic creation and annihilation operators which create and annihilate vibrational quanta of modes with frequency ω_i respectively and the Hamiltonian takes on a very simple form

$$H_0 = \sum_{i=1}^{N}\left(a_i^\dagger a_i + \frac{1}{2}\right)\hbar\omega_i$$

- For a more detailed understanding it is typically necessary to include higher order terms in the Taylor expansion. In the *quartic* approximation, terms up to the fourth derivative of the potential energy are retained

$$\frac{1}{2!}\sum_{pq}\left(\frac{\partial^2 V}{\partial x_p \partial x_q}\right)_{eq} x_p x_q + \frac{1}{3!}\sum_{pqr}\left(\frac{\partial^3 V}{\partial x_p \partial x_q \partial x_r}\right)_{eq} x_p x_q x_r + \frac{1}{4!}\sum_{pqrs}\left(\frac{\partial^4 V}{\partial x_p \partial x_q \partial x_r \partial x_s}\right)_{eq} x_p x_q x_r x_s$$

- The aim of our project is to develop a method to solve this *anharmonic* problem using coupled cluster techniques where terms beyond the harmonic approximation are treated as a perturbation.
- Here we present the first steps towards a systematic solution of ground and excited states of such a system using coupled cluster techniques applied to the resulting time-independent Schrödinger equation.

Coupled Cluster Approach (CC)

- In order to illustrate our approach, we will limit this presentation to a set of Harmonic oscillators perturbed by a *quadratic* perturbation. Everything in our derivation can be extended to include higher order, cubic, quartic etc., terms in a systematic way. Using our creation and annihilation operators we can express a general quadratic perturbation by the following perturbing potential

$$V = \frac{1}{2}\sum_{ij=1} A_{ij} a_i a_j + \frac{1}{2}\sum_{ij=1} A_{ij}^* a_i^\dagger a_j^\dagger + \sum_{ij=1} B_{ij} a_i^\dagger a_j + \sum_{ij=1} C_{ij} a_i a_j^\dagger$$
$$\mathbf{A} = \tilde{\mathbf{A}}\ ;\ \mathbf{B} = \mathbf{B}^\dagger\ ;\ \mathbf{C} = \mathbf{C}^\dagger$$

- Our goal is to solve the resulting time-independent Schrödinger equation for *N* oscillators

$$\left(H_0 + V\right)\left|\psi\right\rangle = E\left|\psi\right\rangle$$
$$H_0 = \sum_{i=1}^{N}\left(a_i^\dagger a_i + \frac{1}{2}\right)\hbar\omega_i$$

- In the EOM-CC approach we first express the ground state in terms of a coupled cluster expansion so that for the ground state the Schrödinger equation reads

$$H\left|\tilde{0}\right\rangle = He^T\left|0\right\rangle = \tilde{E}_0 e^T\left|0\right\rangle = \tilde{E}_0\left|\tilde{0}\right\rangle$$
$$e^{-T}He^T\left|0\right\rangle = \tilde{E}_0\left|0\right\rangle$$

- In general, the cluster operator consists of all possible excitation of the system

$$T = T_1 + T_2 + T_3 + \ldots = \sum_k t_k a_k^\dagger + \frac{1}{2!}\sum_{kl} t_{kl} a_k^\dagger a_l^\dagger + \frac{1}{3!}\sum_{klm} t_{klm} a_k^\dagger a_l^\dagger a_m^\dagger + \ldots$$

- Via the use of the Baker-Campbell-Hausdorff formula, we can define an *effective* Hamiltonian (H-bar)

$$\bar{H} \equiv e^{-T}He^T = \left(He^T\right)_c$$

- Where the "c" indicates that only contracted (or connected) terms are retained.
- The coupled cluster amplitudes can now be obtained from a set of coupled non-linear equations resulting from projections of the Schrödinger equation

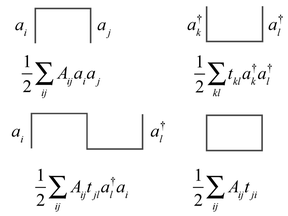
$$\left\langle 0\right|a_i\bar{H}\left|0\right\rangle = 0$$
$$\left\langle 0\right|a_i a_j\bar{H}\left|0\right\rangle = 0$$
$$\vdots$$

- And the ground state energy is obtained from

$$\tilde{E}_0 = \left\langle 0\right|\bar{H}\left|0\right\rangle$$

Diagrammatics and Example of Operating Equations

- We express the Hamiltonian and the coupled cluster operator in diagrammatic form and by deriving diagrammatic rules we can effectively calculate the necessary terms in our equations
- As an example, the following diagrams illustrate how two operators (top) can be connected in two ways, giving rise to two required terms in the EOM-CC operating equations.



- In the case of a quadratic perturbation we can show that the *exact* solution can be obtained by only including double excitations in the cluster operator.
- The resulting non-linear equations for the amplitudes are solved iteratively and a simple expression is found for the perturbed ground state energy.

$$A_{ij}^* + \left(\hbar\omega_i t_{ij} + \hbar\omega_j t_{ij}\right) + \left(\mathbf{DT}_2\right)_{ij} + \left(\mathbf{T}_2\mathbf{DT}_2\right)_{ij} = 0 \quad ; \quad \mathbf{D} = \mathbf{B} + \mathbf{C}^*$$
$$\tilde{E}_0 = E_0 + \frac{1}{2}Tr\left(\mathbf{AT}_2\right)$$

- In the case of a *quartic* perturbation there is no restriction on the excitation level of the cluster operator and it has to be truncated at some level to give a finite number of coupled equations.

EOM-CC Excited States

- In the EOM-CC method, excited states are obtained by diagonalizing the effective Hamiltonian (non-hermitean) matrix in the basis of the *unperturbed* harmonic oscillator states. Symbolically we can represent this by blocks involving the ground, first, second, etc. excited states

$$\bar{\mathbf{H}} = \begin{pmatrix} \left\langle 0\right|\bar{H}\left|0\right\rangle & \left\langle 0\right|\bar{H}\left|1\right\rangle & \left\langle 0\right|\bar{H}\left|2\right\rangle & \cdots \\ \left\langle 1\right|\bar{H}\left|0\right\rangle & \left\langle 1\right|\bar{H}\left|1\right\rangle & \left\langle 1\right|H\left|2\right\rangle & \cdots \\ \left\langle 2\right|\bar{H}\left|0\right\rangle & \left\langle 2\right|\bar{H}\left|1\right\rangle & \left\langle 2\right|\bar{H}\left|2\right\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

- In the case of *quadratic* perturbation, this matrix simplifies and the eigenvalues can be written off directly from the diagonal elements of the matrix!

$$\bar{\mathbf{H}} = \begin{pmatrix} \left\langle 0\right|\bar{H}\left|0\right\rangle & \left\langle 0\right|\bar{H}\left|1\right\rangle & \left\langle 0\right|\bar{H}\left|2\right\rangle & \cdots \\ 0 & \left\langle 1\right|\bar{H}\left|1\right\rangle & \left\langle 1\right|H\left|2\right\rangle & \cdots \\ 0 & 0 & \left\langle 2\right|\bar{H}\left|2\right\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

- When considering cubic, quartic… perturbations we will have to truncate the space in order to generate a finite matrix which to diagonalize.
- We note that the result above is directly linked to a Bogoliubov transformation of our original creation and annihilation operators resulting in the ability to express the perturbed Hamiltonian in a new set of harmonic oscillators

$$b_i^\dagger = \sum_j F_{ij} a_j^\dagger + \sum_j G_{ij} a_j \qquad F = (1 - t_2^* t_2)^{-1/2} \qquad G = -(1 - t_2^* t_2)^{-1/2} t_2$$
$$b_i = \sum_j F_{ij}^* a_j + \sum_j G_{ij}^* a_j^\dagger \qquad H = \sum_{i=1}^{N}\left[\left(b_i^\dagger b_i + \frac{1}{2}\right)\hbar\tilde{\omega}_i + \Delta_i\right]$$

Conclusions and Future Work

We have presented the results of our first steps towards calculating ground and excited state energies of a set of coupled oscillators using coupled cluster techniques. The process presented was illustrated for a simple quadratic perturbation, to which the exact solution is known. Our next steps involve implementing the method for the case of cubic and quartic perturbations and benchmarking the method with respect to existing calculations. Future work will include the application of the method to realistic physical systems, e.g. the case of anharmonic molecular vibrations where the necessary potential parameters can be obtained.

Quadratic Perturbation of Single Oscillator

- The graphs below show the output from our Python code for the case of a quadratic perturbation of a single harmonic oscillator.
- The top graphs shows the iterative convergence of the single cluster amplitude and the corresponding convergence of the ground state energy. In this simple case the convergence is straightforward something which is not guaranteed in more general cases.
- Given the form of our EOM effective Hamiltonian matrix we would expect to see the appearance of a set of equally spaced eigenvalues reflecting the perturbed frequency as the coupled cluster amplitude converges. This is illustrated in the third graph.
- Finally, the bottom graph shows the behavior of the eigenvalues of the effective Hamiltonian as a function of iteration step, illustrating the fact that we are dealing with a non-hermitean matrix, resulting in the appearance of pairs of complex eigenvalues, which gradually move to the real axis as the ground state coupled cluster amplitude converges. In this particular case we are guaranteed to get real eigenvalues since our method in principle provides the exact solution for the ground state as well for any truncation level of the space used in the diagonalization of the effective Hamiltonian.