

A Journey into Quantum Molecular Dynamics and DFT

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Outline

- 1 History of Quantum Molecular Dynamics
- 2 History of Density Functional Theory (DFT)
- 3 Methods of QMD
 - Semi-Epirical (MNDO, AM1, Tight-Bending)
 - Post-Hartree-Fock (MP2-MD, CCSD-MD)
 - PIMD
- 4 General Conclusions
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Origins of Molecular Dynamics (MD)

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- However, interest in the evolution of N-body systems dates back to the 17th century with Isaac Newton, focusing mainly on celestial mechanics.
- Many key numerical algorithms were created before computers. For example, the **Verlet integration algorithm**, the most common today, was used as early as 1791 by Jean Baptiste Joseph Delambre.

Pre-Computational Methods

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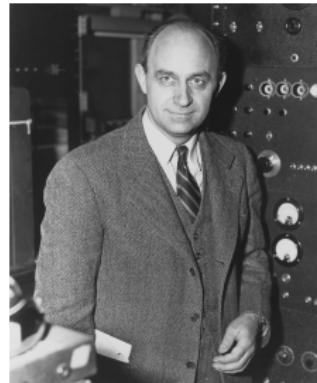
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The Fermi-Pasta-Ulam-Tsingou Problem

To understand the origin of irreversibility, Enrico Fermi and his collaborators used the **MANIAC I** computer in 1953 to simulate the time evolution of a many-body system.

Los Autores del Problema FPU



Enrico Fermi



John Pasta

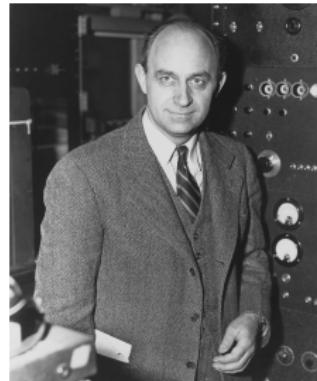


Stanislaw Ulam



Mary Tsingou

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FPU Problem Graph

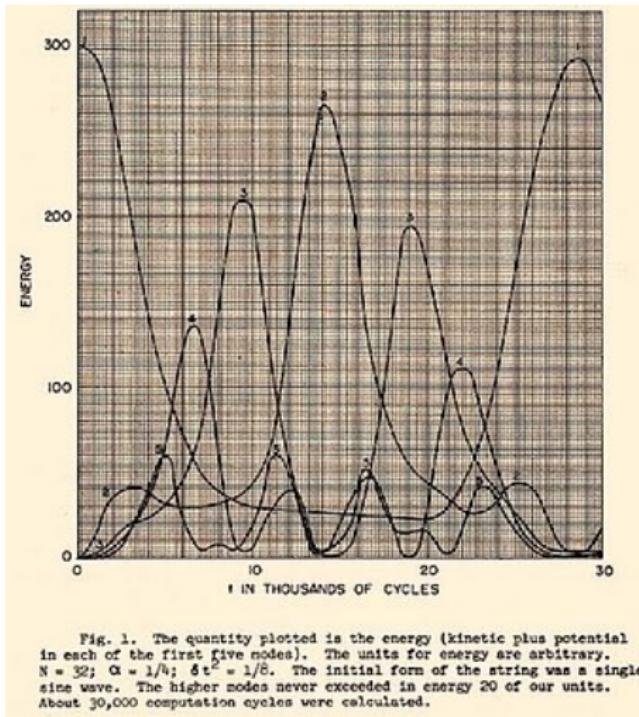


Figure: Energy vs. time for one of the first N-body systems simulated by Fermi, showing unexpected and non-irreversible behavior.

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The Legacy of the Lennard-Jones Potential

Today, it remains one of the most widely used potentials for describing simple substances and as a component of more complex force fields.

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- ④ **Iteration:** Steps 2 and 3 are repeated for the time required to observe the system's evolution.

MD Algorithm Graph

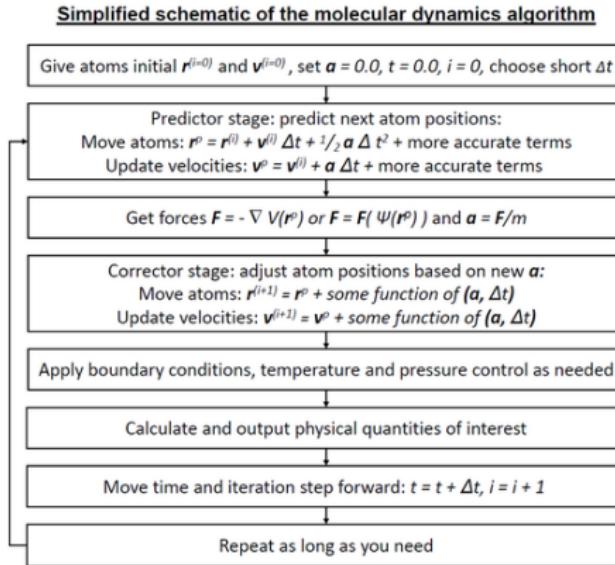


Figure: Simplified schematic of the Molecular Dynamics algorithm.

From Classical to Quantum MD

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The Birth of Quantum Molecular Dynamics

This idea gives rise to **Ab Initio Molecular Dynamics (AIMD)**, where forces are obtained by solving the Schrödinger equation for the electrons at each atomic configuration.

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Impact

The Car-Parrinello method turned quantum molecular dynamics into a practical and predictive tool, and it remains one of the pillars of the field today.

Two Main Approaches in AIMD

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Born-Oppenheimer Molecular Dynamics (BOMD)

- Strictly adheres to the Born-Oppenheimer approximation.
- **Calculates the electronic ground state** accurately at each time step.
- It is conceptually simpler and very robust.
- It generally allows for larger time steps, but each step is more computationally expensive.

Car-Parrinello Molecular Dynamics (CPMD)

- Propagates the nuclei and electronic orbitals simultaneously.
- The electrons are **not exactly in the ground state** at each step, but they remain close to it.
- It is computationally more efficient per time step.
- It requires smaller time steps to maintain adiabaticity.

The Classical Limitation and the Quantum Leap

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The Quantum Need

To simulate these phenomena, forces on the atoms must be calculated from the system's electronic structure using quantum mechanics. This gives rise to **Quantum Molecular Dynamics (QMD)** or **Ab Initio Molecular Dynamics (AIMD)**.

I. Origins: The Precursors

The Density as a Basic Variable

- The earliest density-based methods trace back to the Thomas, Fermi, and Dirac papers (1927–1930).
- **The Thomas-Fermi-Dirac model** described atoms based purely on the electron density $n(\mathbf{r})$.
- The motivation was to find "approximate practical methods" to solve the complicated quantum mechanical equations (Dirac, 1929).
- Limitation: The Thomas-Fermi model has severe deficiencies, such as the inability to predict molecular or solid binding.

II. Modern Density Functional Formalism (HK)

The Hohenberg-Kohn Theorems (1964)

- HK Theorem 1: The external potential $V_{\text{ext}}(\mathbf{r})$ (and thus the full Hamiltonian) is uniquely determined by the ground-state electron density $n(\mathbf{r})$.
- HK Theorem 2: A universal functional for the energy, $E[n]$, exists, and the correct ground-state density minimizes this Functional.

$$E[n, V_{\text{ext}}] = F[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} \quad (\text{Variational Principle})$$

- This formal grounding eliminated the need for the complicated $3N$ -dimensional wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$.

III. The Kohn-Sham Scheme and Approximations

The Practical Method (1965)

- The Kohn-Sham (KS) scheme introduced a non-interacting auxiliary system that produces the exact ground-state density $n(\mathbf{r})$ of the real interacting system.
- This turns the many-body problem into a set of solvable single-particle equations (Kohn-Sham equations).
- The complexity is now contained in the exchange-correlation functional $E_{xc}[n]$.
- Key Approximations:
 - Local Density Approximation (LDA): Based on the homogeneous electron gas.
 - Generalized Gradient Approximation (GGA): Introduced dependence on the density gradient, ∇n .

IV. The Rise to Prominence (Post-1990)

- Widespread application, particularly in chemistry and materials science, grew astonishingly after 1990.
- The number of publications citing DFT/DF increased dramatically, marking a huge success story (Fig. 1).
- Crucial Developments:
 - Car-Parrinello Molecular Dynamics (1985): Combined DFT with MD, enabling efficient study of structures and reactions.
 - Improved Functionals: Development of GGAs and hybrid functionals (e.g., incorporating Hartree-Fock exact exchange).
- A 1991 conference in Menton is cited as a major turning point for acceptance among chemists.

V. Current Status and Applications

A Standard Tool in Modern Science

- DFT is now well-established in condensed matter physics and has a significant presence in theoretical chemistry.
- It is particularly valuable for calculating the total energy (E) and energy surfaces $E(\mathbf{R}_i)$, which are essential for determining ground-state structures and chemical reaction paths.
- DFT allows calculations of complex systems in biochemistry and materials science that were "far beyond expectations" in 1990.

VI. Challenges and Future Outlook

Quo Vadis? (Whither Goest Thou?)

- Despite its success, prominent practitioners have raised concerns about the future ("best of times and the worst of times").
- **The Central Problem:** The lack of a systematic way to improve the Exchange-Correlation functional (E_{xc}).
- **Current Challenges:**
 - Accurately describing **Dispersion (van der Waals) interactions.**
 - Treating "**Strongly correlated**" systems.
 - The proliferation of hundreds of approximate functionals makes choosing the "best" one ambiguous and risks a "semi-empirical" view of the theory.
- The field is continually exploring extensions, such as combining DFT with Density Matrix Functional Theory (DMFT) or Quantum Monte Carlo (QMC).

VII. Conclusion

- DFT is a huge success story, having moved from theoretical origins to a mainstream computational tool due to the work of Hohenberg, Kohn, and Sham and the subsequent development of reliable functional approximations.
- Its widespread acceptance came after 1990, driven by its efficiency and ability to handle large systems, a goal anticipated by Dirac in 1929.
- The future of DFT rests on the continuing development of accurate, universal, and physically sound exchange-correlation functionals.

Methods for Electronic Dynamics

By Propagation Algorithm

Born-Oppenheimer Molecular Dynamics (BOMD)

Car-Parrinello Molecular Dynamics (CPMD)

Ehrenfest Molecular Dynamics(EMD)

Methods for Electronic Dynamics

By Level of Electronic Theory

Density Functional Theory (DFT-MD)

Wavefunction Theory (WFT-MD)

Hartree-Fock (HF-MD)

Post-Hartree-Fock (MP2-MD, CCSD-MD)

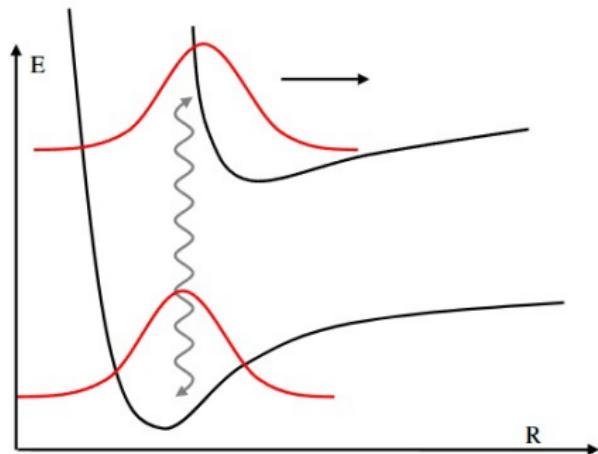
Semi-empirical Methods (SE-MD)

Paper Title

Born-Oppenheimer Molecular Dynamics

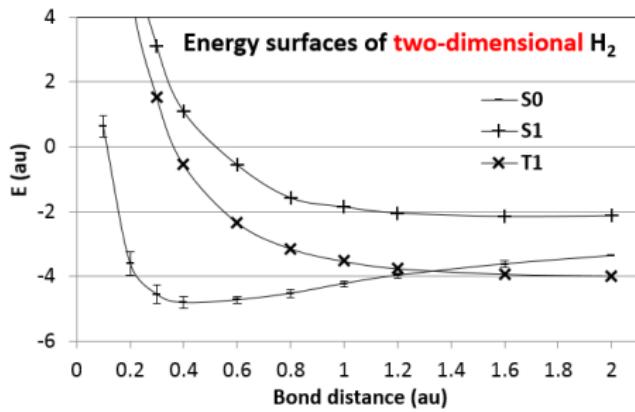
The Core Idea

- Nuclei are fixed.
Electrons move.
- The huge mass
difference is key.



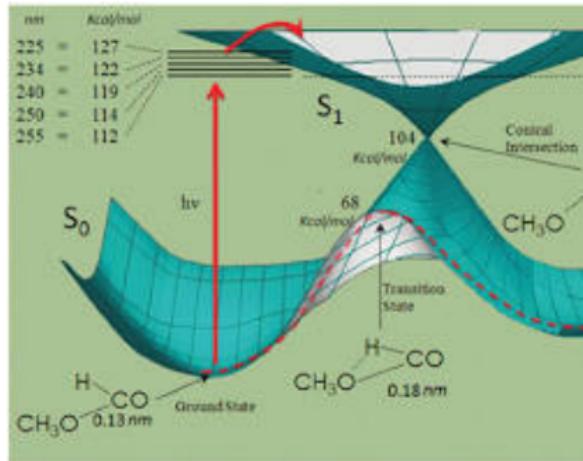
The Result

- Defines the concept of molecular structure.
- It generates Potential Energy Surfaces (PES).



The Limitation

- Fails when electronic states are coupled.
- Not suitable for most photochemical reactions.

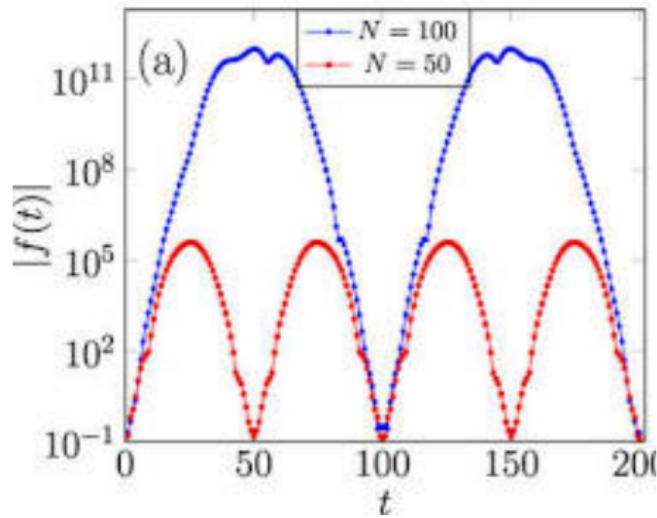


Paper Title

Ehrenfest Molecular Dynamics

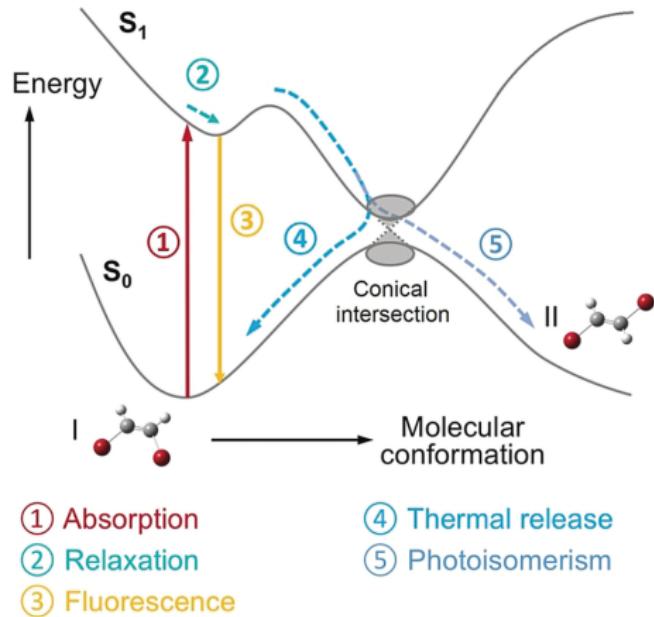
The Core Idea

- Nuclei are treated as classical particles.
- Electrons are treated quantum mechanically.



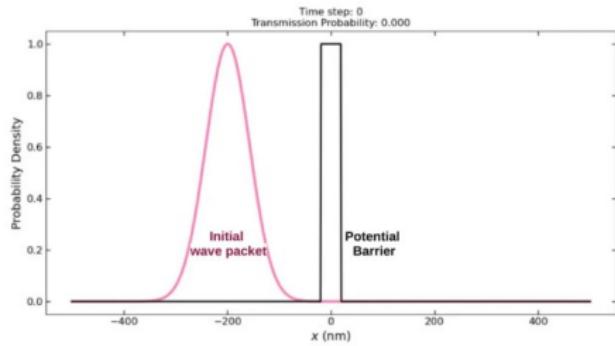
The Application

- Simulates non-adiabatic processes and transitions.
- Models molecular relaxation after photoexcitation.



The Limitation

- It is a "mean-field" approximation.
- Fails to describe wavepacket branching.

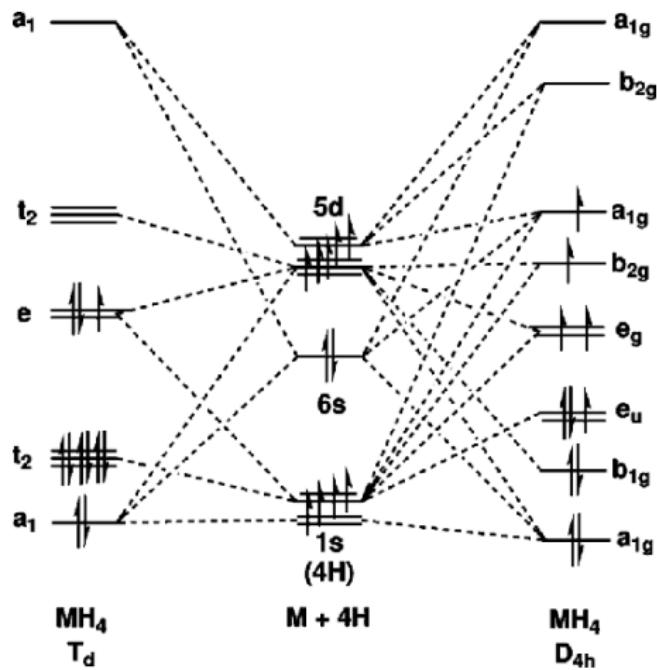


Paper Title

Møller-Plesset Molecular Dynamics

The Core Idea

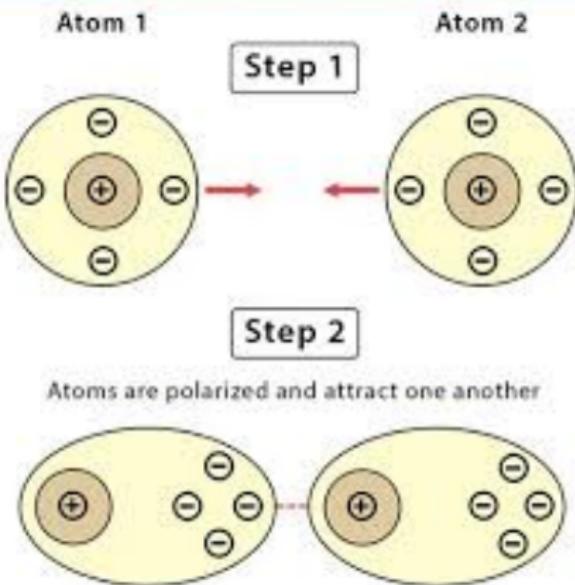
- Improves upon the Hartree-Fock method.
- Includes instantaneous electron correlation.



The Application

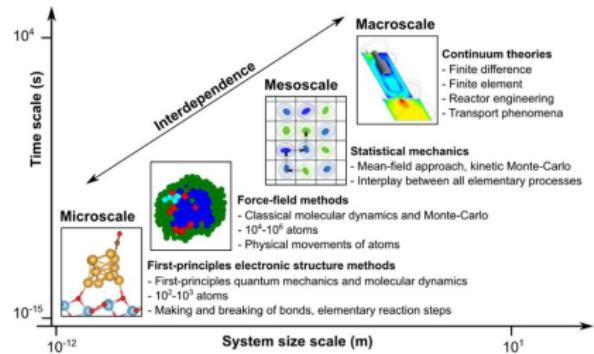
Van der Waals Forces

- Accurately describes van der Waals forces.
- Crucial for non-covalent interactions.



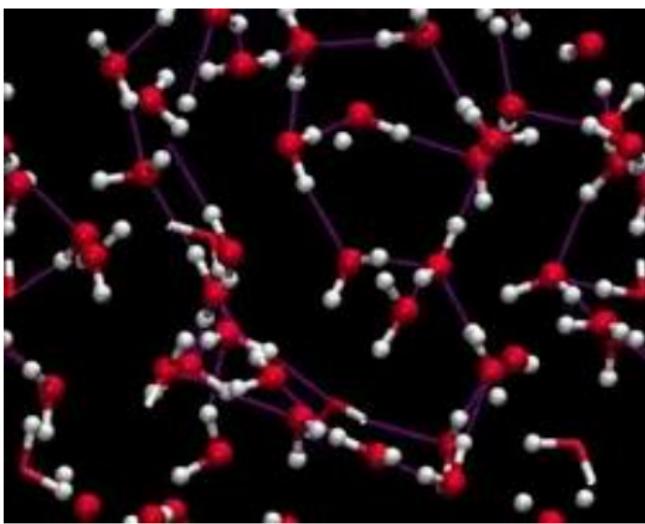
The Limitation

- Computationally expensive, scaling as N^5 .
- Can fail for strongly correlated systems.



Water simulation with MP2

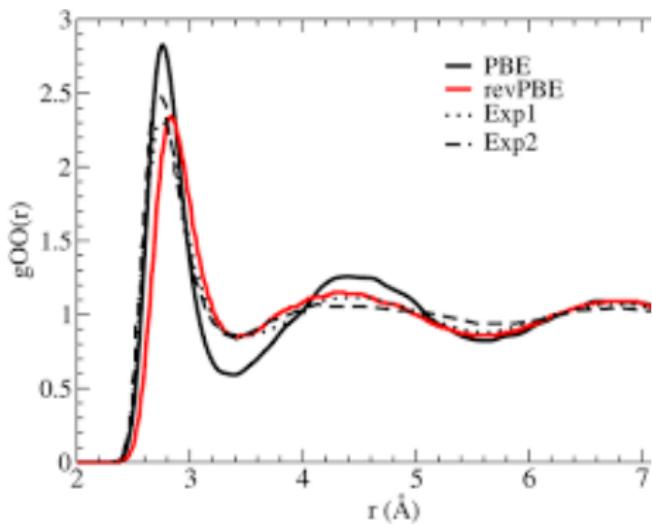
- First ab initio MD of water with MP2.
- Overcame immense computational cost.



https://youtu.be/Z174NCVbA5A?si=_vw8W1vdoYTN6lkV

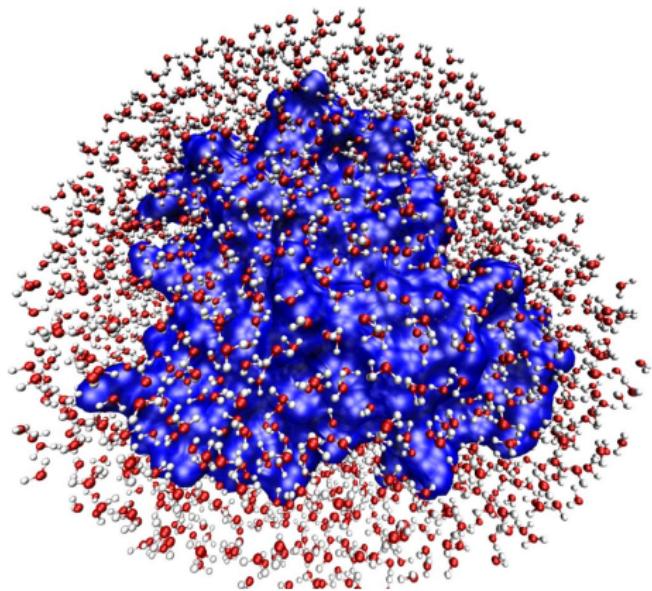
The Result

- Produced a more realistic water structure.
- Matched experimental RDF data better.



The Impact

- Set a new benchmark for DFT methods.
- Proved correlation is essential for water.

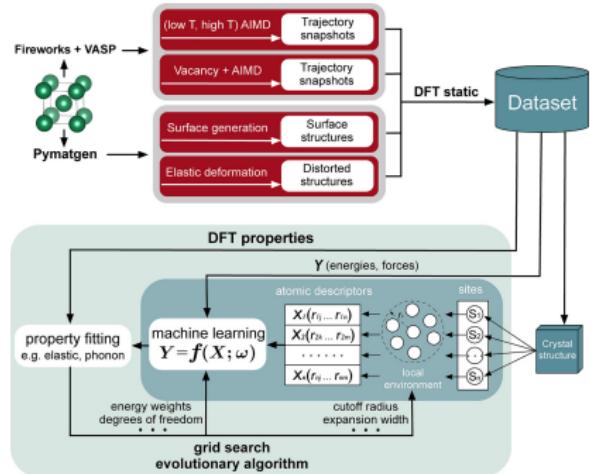


Paper Title

Coupled Cluster Singles and Doubles Molecular Dynamics

The Method

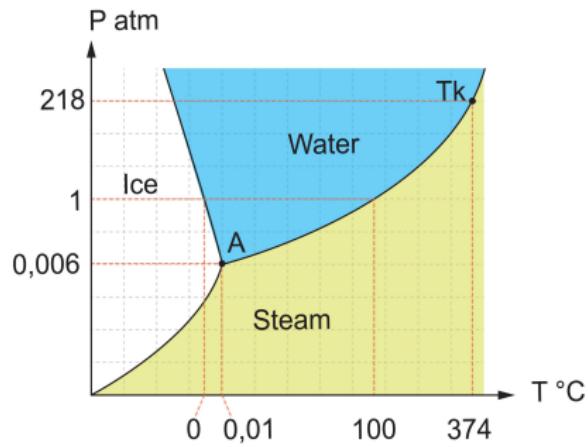
- Uses Machine Learning for MD simulations.
- Achieves "gold standard" CCSD(T) accuracy.



The Result

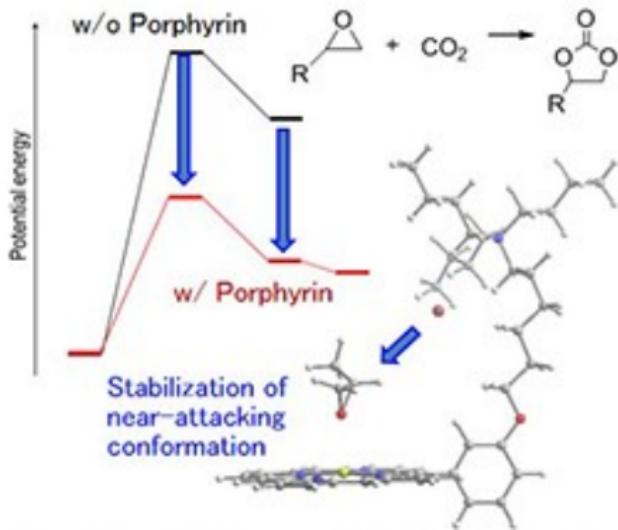
- Accurately reproduced water's phase diagram.
- Captured water's famous density anomaly.

Triple phase diagram of water



The Future

- Revolutionizing simulations in materials science.
- Enables gold-standard accuracy for large systems.



Paper Title

Ground State of Molecules The MNDO Method Approximation and Parameters

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- It is a **semiempirical** method, meaning it combines theory with experimental parameters.
- Its theoretical basis is the **NDDO** (Neglect of Diatomic Differential Overlap) approximation, which is more rigorous than previous methods like INDO or CND0.

Approximation I: One-Center Terms

Energies and Repulsions on a Single Atom

- The terms that describe the energy of an electron in an atom ($U_{\mu\mu}$) and the repulsion between electrons on the same atom ($g_{\mu\nu}$, $h_{\mu\nu}$) are not calculated theoretically.

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- Instead, they are derived by fitting the calculations to **experimental spectroscopic data** for the atom and its ions.
- This implicitly introduces an **electron correlation** effect, as the fitted values are smaller than the theoretical ones.

Approximation II: Two-Center Repulsion

The Key Innovation of MNDO

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- Each multipole is in turn represented as a simple configuration of **point charges**.
- The final repulsion energy is calculated by summing the interactions between these point charges using a semiempirical formula.

Approximation III: Chemical Bonding

Core-Core and Resonance Interactions

- **Core-Core Repulsion:** The repulsion between the nuclei and inner-shell electrons ("cores") is modeled with a function that blends charge repulsion with an adjustable exponential term.

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- **Core-Core Repulsion:** The repulsion between the nuclei and inner-shell electrons ("cores") is modeled with a function that blends charge repulsion with an adjustable exponential term.
- **Resonance Integrals ($\beta_{\mu\lambda}$):** These are responsible for most of the bonding energy. They are assumed to be proportional to the overlap of the atomic orbitals, with a constant that depends on atomic parameters.

The Parametrization Process

Fitting to Experimental Reality

- The mathematical expressions in the method contain a series of **atomic parameters** (ζ , U_{ss} , β_p , etc.).

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- The values of these parameters are not derived from theory. They are obtained through a **nonlinear least-squares optimization process**.
- The parameters are adjusted until the calculated properties (heats of formation, geometries, etc.) for a set of standard molecules match their **experimental values** as closely as possible.

Paper Title

AM1: A New Method General Purpose Quantum Mechanical Molecular Model

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 - Chemical reactions and their mechanisms.
- It was created as an alternative to *ab initio* methods, which were prohibitively expensive in terms of computation time for molecules of real chemical interest.

The Predecessor: Weaknesses of MNDO

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Main Flaws of MNDO

- Inability to correctly reproduce **hydrogen bonds**.
- Overestimation of interatomic repulsions, leading to errors in:
 - Sterically hindered molecules (e.g., neopentane).

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- Capable of genuinely modeling **hydrogen bonds**.
- More accurate estimates of **activation energies**.
- Better treatment of **hindered molecules** (e.g., neopentane) and those with ring strain (e.g., cubane).

Tight-Bending

Paper Title

Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties

The Limits of Standard Tight-Binding

Standard Tight-Binding (TB) is a computationally fast method derived from Density-Functional Theory (DFT).

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- However, it has a significant limitation: it is a **non-self-consistent** method.
- This means it cannot account for the transfer of charge between different types of atoms. This leads to failures in polar or heteronuclear systems and limits the method's overall transferability.

The SCC-DFTB Solution: Self-Consistent Charges

The Self-Consistent-Charge (SCC) method extends the standard approach by allowing the system's charges to re-distribute.

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- This term correctly describes long-range Coulomb interactions between charges and includes on-site self-interaction effects related to an atom's chemical hardness (the Hubbard parameter U).
- The method then iterates, adjusting the charges and recalculating the energy until a self-consistent, minimum-energy solution is found.

Why It Matters: The Payoff of SCC-DFTB

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- **Efficiency is Maintained:** The self-consistent cycle is very fast, typically converging in just 3-5 iterations. The method remains orders of magnitude faster than ab initio calculations.

Paper Title

On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum Field Theoretical Methods

Coupled Cluster (CC) Method

The Problem: Electron Correlation

Standard methods like Hartree-Fock ignore that electron movements are correlated. The CC method aims to calculate this **correlation energy**.

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The Central Idea: The Exponential Ansatz

It expresses the exact wavefunction $|\Psi\rangle$ by applying an exponential "cluster operator" $e^{\hat{T}}$ to the Hartree-Fock wavefunction $|\Phi\rangle$:

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle$$

How Coupled Cluster Works

- The **cluster operator** \hat{T} is a sum of excitation operators ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$), where \hat{T}_1 creates single excitations, \hat{T}_2 creates double excitations, and so on.

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- The method uses tools from **quantum field theory** (hole-particle formalism, Wick's theorem) to solve for the amplitudes of these excitations.
- Its key advantage over Configuration Interaction (CI) is that truncating at \hat{T}_2 (CCSD) still includes the most important effects of quadruple excitations, making the method very efficient and **size-extensive**.

CCSD vs GCCSD

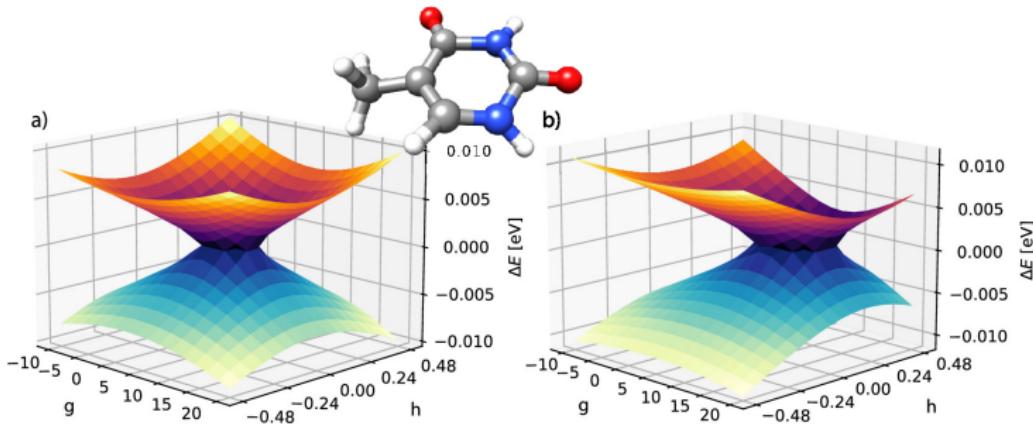


Figure: Superficies de energía potencial S1 y S2 en timina calculadas con CCSD (a) y GCCSD (b).

Trajectory Surface Hopping (TSH)

Multi-Configuration Time-Dependent Hartree (MCTDH)

Paper Title

Molecular dynamics with electronic transitions

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- The electronic state changes, and the forces governing the atoms change drastically. The system effectively jumps to a **new potential energy surface**.
- We need a method that can simulate classical atomic trajectories while allowing for quantum electronic transitions.

The Trajectory Surface Hopping (TSH) Solution

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- **Quantum Electrons:** The time-dependent Schrödinger equation is solved for the electrons along this trajectory, yielding the probability of being in *any* of the available electronic states.

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- A random number is used to make a stochastic decision: **to hop or not to hop.**
- If a hop occurs, the atoms' velocities are instantly adjusted to conserve total energy, and the trajectory continues on the new potential energy surface.

Methods Including Nuclear Quantum Effects

Path Integral Molecular Dynamics (PIMD)

- Centroid Molecular Dynamics (CMD)
- Ring Polymer Molecular Dynamics (RPMD)

Wave Packet Propagation

PIMD (Path Integral Molecular Dynamics)

Paper Title

Study of an F center in molten KCl

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- Consider an electron (a quantum particle) dissolved in a bath of classical ions, like molten salt.
- The electron does not have a fixed position; its quantum nature means it is "fuzzy" and delocalized.
- How can we combine the quantum statistical mechanics of the electron with the classical statistical physics of the ions in a single simulation?

The Path Integral Solution: A Quantum-Classical Isomorphism

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- Every bead also interacts with the external potential created by the classical particles.
- This mapping becomes exact as the number of beads (P) approaches infinity. In practice, a finite but sufficiently large P is used.

Simulating the Necklace: PIMD in Action

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- This allows us to calculate quantum properties like kinetic energy and study phenomena like electron localization, all within a classical simulation framework.

CMD (centroid molecular dynamics)

Paper Title

The formulation of quantum statistical mechanics based on the Feynman path centroid density. II. Dynamical properties

Beyond Static Properties: The Challenge of Quantum Dynamics

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- We need a way to extract real physical evolution from the path integral framework.

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- However, the centroid does not move on the classical potential. It evolves on a **quantum potential of mean force** (V_c).
- This "centroid potential" is an effective potential averaged over all the quantum fluctuations of the polymer beads, and it implicitly includes quantum effects like zero-point energy and tunneling.

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Key Advantage

The computational cost of a CMD simulation scales in the same way as a purely classical simulation, making it a powerful tool for studying quantum

RPMD for Real-Time Quantum Correlation Functions

- **The Problem:** The exact calculation of quantum real-time correlation functions is still considered "a very difficult problem".
- **General Approach:** A number of methods have been proposed to include short-time quantum mechanical effects in classical molecular dynamics simulations. These methods typically combine an exact treatment of the quantum Boltzmann operator with an approximate treatment of the real-time evolution based on classical mechanics.
- **The Proposed Method (RPMD):** We propose an approximate method, based on path integral (Parrinello-Rahman) molecular dynamics, for calculating **Kubo-transformed real-time correlation functions** involving position-dependent operators.
- **Core Idea:** Exploit the isomorphism between the path integral representation of the quantum mechanical partition function and the classical partition function of a fictitious ring polymer.

Methodology: Kubo Transform and Dynamics

- **Object of Interest:** The method focuses on the Kubo-transformed correlation function, $\tilde{C}_{AB}(t)$.
 - This function is appealing because it has the same symmetries as a classical correlation function.
- **Initial Condition ($t = 0$):** The $t \rightarrow 0$ limit of $\tilde{C}_{AB}(t)$ coincides with a purely classical phase space average $\langle A_n(x)B_n(x) \rangle_n$ calculated for the fictitious ring polymer system.
- **Time Evolution:** To extend this result to times $t > 0$, the method uses the classical dynamics generated by the ring polymer Hamiltonian $H_n(p, x)$.
 - The resulting correlation function, $\langle A(0)B(t) \rangle_n$, is calculated via integration over initial phase space variables evolved using the classical equations of motion.
- **Symmetry Guarantee:** The classical ring-polymer correlation function $\langle A(0)B(t) \rangle_n$ maintains the crucial symmetries of $\tilde{C}_{AB}(t)$, including the quantum mechanical detailed balance condition.

Key Analytical Results and Advantages

- **RPMD is Exact at $t = 0$:** The resulting correlation functions coincide with the exact quantum mechanical result in the limit as $t \rightarrow 0$ (for sufficiently large n).
- **The Harmonic Limit:** RPMD gives the exact quantum mechanical result $\tilde{C}_{AB}(t)$ for all times t in a harmonic potential, provided that one or both operators ($A(\hat{x})$ or $B(\hat{x})$) are linear functions of position.
 - For the position autocorrelation function $\tilde{C}_{xx}(t)$, the classical limit ($n = 1$ polymer bead) is already exact in the harmonic case.
- **Consistent Improvement:** The RPMD correlation functions are consistently better than those given by purely classical molecular dynamics.
 - This improvement is **most apparent in the low-temperature regime** where quantum statistics are critically important.
- **Computational Efficiency:** RPMD requires less computational work compared to the related centroid molecular dynamics method, yet its results are only marginally less accurate for tested problems.

Limitations and Summary

- **Short-Time Focus:** The method is designed primarily to give an accurate approximation to the quantum mechanical correlation function for times on the order of the thermal time ($\beta\hbar$).
- **Missing Quantum Dynamics:** The neglect of quantum phase information in the subsequent dynamics is clearly undesirable.
- **Failure for Long-Time Coherences:** The method misses long-time quantum coherence effects that arise in simple one-dimensional anharmonic systems (e.g., the quartic oscillator).
 - This failure is expected, as the method does not contain the phase information needed to capture long-time quantum oscillations.
 - The method performs well only in situations where quantum effects in the dynamics are comparatively unimportant.
- **Summary:** RPMD successfully includes short-time quantum effects stemming from the Boltzmann operator, providing a consistent improvement over classical MD, especially at lower temperatures.
- **Future Work:** It will be interesting to test RPMD in condensed phase applications, such as calculating the infrared absorption spectrum of liquid water.

Hybrid Methods

Quantum Mechanics / Molecular Mechanics (QM/MM)

Context and Hartree's Approximation (1928)

- The non-relativistic quantum mechanical N -electron problem is formulated by the Schrödinger wave equation in $3N$ -dimensional configuration space .
- An exact solution of this equation presents insurmountable mathematical difficulties, necessitating the reliance on approximation methods .
- D. R. Hartree proposed a brilliant approximation method (**the method of self – consistent field**) .
- Hartree's approach assumes that the effects of electrons on one another can be represented by supposing each moves in a central non-Coulomb field of force.
- The method retains the classical concept of the orbit, which lends it great physical interpretability .
- **The Wave Function Ansatz:** Hartree's approach is mathematically equivalent to approximating the wave function Ψ as a simple product of functions of the coordinates of individual electrons :

The Limitation of Hartree's Method and Fock's Refinement (1930)

- The simple product ansatz used by Hartree **does not possess the necessary symmetry properties** required by group theory (except for the ground state of Helium).
- Consequently, Hartree's equations represent only a fairly crude approximation .
- This approximation corresponds to the **neglect of the so – called Exchange Energy** (*Austauschenergie*) .
- V. Fock demonstrated that the optimum solution compatible with describing the atomic state via individual electron wave functions (ψ_i) is not yet reached in the Hartree method .
- **The Improved Ansatz:** A better approximation is achieved by choosing an expression for Ψ that has the correct symmetry .
- Fock's approach utilizes the **variational principle** to establish a system of equations that is more accurate than Hartree's .
- Fock's theory considers the Pauli principle implicitly by influencing the symmetry properties of the wave function.

Fock's Determinant Ansatz and Exchange Terms

- The wave function Ψ must behave like a linear combination of the eigenfunctions corresponding to a given term .
- In the important special case of "**completely degeneracy of the terms system**", Ψ can be approximated by a **product of two determinants**:

$$\Psi = \Psi_1 \Psi_2 \quad [6, 14]$$

- The calculation for this determinant product ansatz was carried out by Fock.
- The resulting equations for the functions $\psi_i(x)$ contain **exchange terms** (*Austauschglieder*).
- **Neglecting these exchange terms leads back to the Hartree system of equations**
- The exchange terms, represented by coefficients with differing indices (e.g., $G_{12}(x)$, $G_{21}(x)$, H_{12} , H_{21}), are generally smaller than diagonal terms (G_{11} , G_{22}) but are significant enough that they should not be neglected.

Structure and Derivation of Fock's Equations

- Both Hartree's equations and Fock's refined equations can be viewed as the **Euler equations of a three-dimensional variational problem**.
- The corresponding action integral for Fock's equations is equal to the total energy E of the atom.
- A characteristic feature preserved in Fock's equations is that the action of the electron on itself ($G_{ii}(x)$) is subtracted from the full potential energy $V(x)$.
- **Energy Expression:** For the example of Helium (*Parhelium*), the energy E is given by $H_{11} + H_{22} + (12|G|12) - (12|G|21)$.
- The integral representing the electron interaction energy involves the term $\rho(x)\rho(x') - [\rho(x, x')]^2$ instead of just the product of charge densities.
- This structure is interpreted to mean that **the electron does not act upon itself**.
- Fock's results show a remarkable similarity with expressions derived by P. Jordan using the method of renewed quantization.

Computational Methods and Expected Accuracy

- **Atomic Units:** Both works utilize atomic units to simplify calculations and eliminate universal constants (e.g., unit of length a_H , unit of charge e , unit of energy e^2/a_H) [23-25].
- Hartree's differential equation for the radial function $P = r\psi$ is $\mathbf{P}'' + [2\mathbf{v} - \epsilon - \mathbf{I}(\mathbf{I} + 1)/\mathbf{r}^2]\mathbf{P} = \mathbf{0}$ [26]. P^2 gives the radial density of charge [27, 28].
- **Integration Technique (Hartree):** Characteristic values of ϵ are found by integrating the wave equation **outwards from** $r = 0$ and **inwards from** $r = \infty$, finding the value of ϵ where the logarithmic derivatives (P'/P or η) fit at an intermediate radius [28, 29].
- Hartree developed exact equations for the variation of a solution with a change in potential (Δv) or energy ($\Delta \epsilon$), which significantly reduces numerical work [30, 31].
- **Accuracy:** Fock anticipates that if the assumption of spherical symmetry is made, the numerical integration of his equations should not be substantially more difficult than Hartree's calculations, but the results are expected to be **considerably more accurate**.

Comparison Summary

Feature	Hartree (1928)	Fock (1930)
Ansatz (Ψ)	Simple Product ($\prod \psi_i$)	Product of Determinants
Symmetry	Incorrect/Crude	Correct/Improved
Exchange Terms	Neglected	Included (Austin)
Variational Basis	Follows from Product Ansatz	Explicit basis for derivation
Expected Accuracy	Crude Approximation	Considerably More Accurate

Key Takeaways:

- Hartree established the method of the self-consistent field, providing a valuable first approximation based on a simple product wave function.
- Fock rigorously derived a more accurate system of equations based on a symmetry-correct determinant ansatz, which automatically incorporates the vital **exchange interaction**.
- The inclusion of exchange terms remedies the omission of the self-interaction in the description of electron energies.

MCTDH: A New Approach to Molecular Dynamics

- **Context:** Approximate methods are needed for solving molecular dynamics in a time-dependent picture, particularly for systems with several degrees of freedom.
- **Problem with Existing Methods:** Known multi-configurational approaches are often based on the use of projection operators.
 - The choice of these projection operators is often unclear .
 - Results explicitly depend on the arbitrary choice of the projection operators, which is unsatisfactory.
- **The New Proposal:** The Multi-Configurational Time-Dependent Hartree (MCTDH) approach is a new time-dependent multi-configurational approach that **does not require** the *a priori* introduction of projection operators .
- **Applicability:** It can be used for n degrees of freedom and for any choice of the number of configurations .

MCTDH Theory: The Ansatz and Constraints

1. General Ansatz: The exact time-dependent wave function Ψ is approximated by the multi-configurational trial function :

$$\Psi(x_1, \dots, x_n, t) = \sum_{j_1, \dots, j_n} a_{j_1 \dots j_n}(t) \prod_{k=1}^n \phi_{j_k}^{(k)}(x_k, t)$$

- The functions $\phi_{j_k}^{(k)}$ are termed "single-particle" functions.
- The numbers of "single-particle" functions (m_k) can be chosen differently for each degree of freedom.

2. Key Constraints:

- **Orthonormality:** The "single-particle" functions must be orthonormal at all times.
- **Minimizing Time Derivative:** Due to redundancy in the ansatz, an additional constraint is applied:

$$\langle \phi_j^{(k)} | \dot{\phi}_j^{(k)} \rangle = 0$$

- **Effect:** This constraint ensures that the time evolution is performed as much as possible by a change in the coefficients $a_{j_1 \dots j_n}$, thereby minimizing the time derivative of the "single-particle" functions and simplifying the working equations.

3. Working Equations: Derived using the Dirac-Frenkel variational principle, resulting in coupled equations for coefficients and "single-particle" function evolution . The working equations are simpler and more transparent than those of other approaches .

Testing and Diagnostics: Fast Convergence

Illustrative Example (2D):

- The approach was tested on a two-dimensional model of coupled oscillators (a modified Hénon-Heiles potential).
- For two degrees of freedom, an exact numerical solution is possible, providing an unambiguous test.
- **Results:** The MCTDH method showed **fast convergence** towards the exact results as the number of configurations (m) was increased. The error was approximately halved for each increment of m .
- **Comparison:** Wave packet plots demonstrated that MCTDH with $m = 3$ and $m = 5$ aligns closely with the exact results, while the single-configuration Time-Dependent Hartree (TDH) result ($m=1$) deviates significantly.

Diagnostic Tool: Natural Weights:

- The eigenvalues of the matrix $A^{(k)\dagger} A^{(k)}$ correspond to the **weights of the natural single-particle functions**.
- These weights provide an **important diagnostic tool**. A small eigenvalue signals convergence with respect to the number of single-particle functions used for that degree of freedom.
- **Utility:** Inspection of these weights is very useful because they indicate whether a sufficient number of functions has been included, *without* the necessity of comparing against an exact calculation.

Summary and Advantages

MCTDH Key Properties:

- The working equations are found to be **well behaved numerically**.
- The propagation conserves both the **norm and the mean energy**.
- Due to the potential for a singular coefficient matrix, regularization (using a small positive number ϵ) is necessary for numerical stability.

Main Advantages:

- **Simplicity:** The derived working equations are simpler and more transparent than those of alternative multi-configurational approaches.
- **No Fixed Projectors:** The approach conserves the orthogonality among the "single-particle" functions without the explicit introduction of fixed (time-independent) projection operators. This avoids reducing the trial space of the propagated wave function.
- **Generalization:** The formalism is generalized to treat any number of degrees of freedom and any desired number of configurations from the beginning.

Outlook:

- The formalism seems easily extendable to a **Multi-Configuration Time-Dependent Hartree-Fock (MCTDHF)** approach for time-dependent problems in quantum chemistry or nuclear physics.

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