Computational quantum molecular dynamics using Hagedorn wavepackets

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work in progress with

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Outline

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Schrödinger equation in semi-classical scaling

$$i\varepsilon \frac{\partial \psi}{\partial t} = H\psi$$

wavefunction $\psi = \psi(x,t), \quad x = (x_1, \ldots, x_N) \in \mathbb{R}^N, \ t > 0$

$$H = T + V$$

Hamiltonian with the kinetic and potential energy operators

$$T = -\sum_{j=1}^{N} \frac{\varepsilon^2}{2m_j} \frac{\partial^2}{\partial x_j^2} \quad \text{and} \quad V = V(x)$$

Computational challenges

- high dimension: $N = 3 \cdot n_{particles}$

- solutions are highly oscillatory with wavelengths $\sim \varepsilon$
- localized with width $\sim \sqrt{\varepsilon}$, with velocity ~ 1

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no grids! (neither full nor sparse)

Rescue?

wavefunction is well approximated by

$$\text{complex Gaussian} \times \text{polynomial}$$

$\longrightarrow$ Hagedorn wavepackets

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Gaussian wavepackets in Hagedorn's parametrization

$$\varphi_0[q,p,A,B](x) = (\pi\varepsilon)^{-N/4}(\det A)^{-1/2} \times \exp\Big(\frac{i}{2\varepsilon}(x-q)^T BA^{-1}(x-q) + \frac{i}{\varepsilon}p^T(x-q)\Big),$$

$q \in \mathbb{R}^N$ position, $p \in \mathbb{R}^N$ momentum

A, B complex $N \times N$ matrices satisfying

$$A^T B - B^T A = 0$$
$$A^* B - B^* A = 2iI$$

Consequences: A and B are invertible, and BA^{-1} is complex symmetric with positive definite imag. part: $\operatorname{Im} BA^{-1} = (AA^*)^{-1}$

Hagedorn 1980

Hagedorn wavepackets

L^2-orthonormal set of functions $\varphi_k(x) = \varphi_k[q, p, A, B](x)$ for multi-indices $k = (k_1, \ldots, k_N)$, constructed recursively: define the *raising operator*

$$\mathcal{R} = (\mathcal{R}_j) = \frac{1}{\sqrt{2\varepsilon}} \Big(B^*(x - q) + A^*(-i\varepsilon\nabla_x - p) \Big)$$

With $\langle j \rangle = (0 \ldots 1 \ldots 0)$ the jth unit vector, set

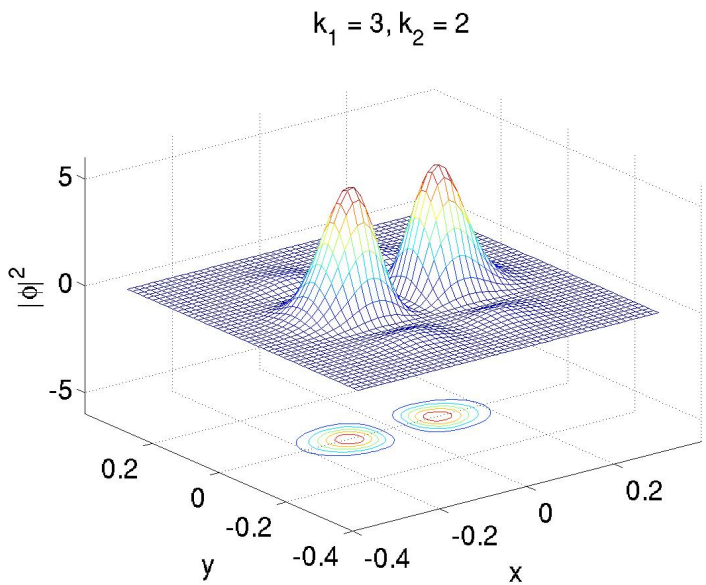
$$\varphi_{k+\langle j \rangle} = \frac{1}{\sqrt{k_j + 1}} \mathcal{R}_j \varphi_k \,.$$

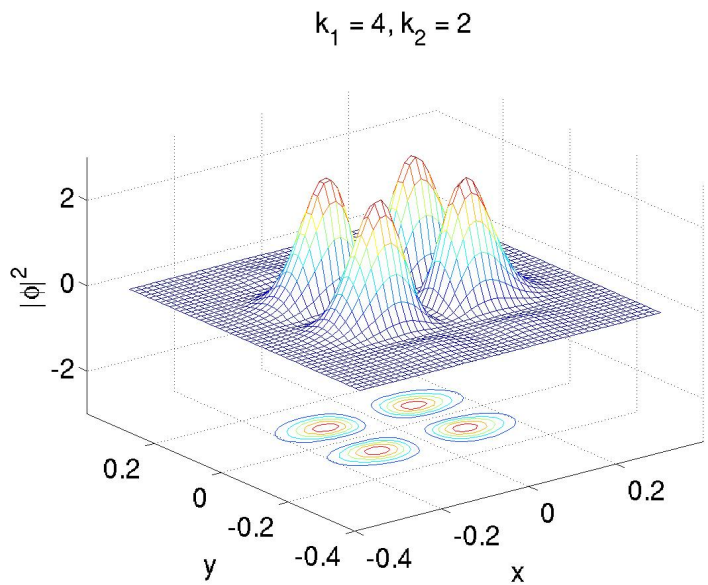
φ_k are polynomials of degree $k_1 + \cdots + k_N$ multiplied with the Gaussian φ_0 ($N = 1$: Gauss-Hermite).

Hagedorn 1998

Recursive evaluation

$$A\left(\sqrt{k_j+1}\,\varphi_{k+\langle j\rangle}(x)\right)_{j=1}^{N} = \sqrt{\frac{2}{\varepsilon}}\,(x-q)\varphi_k(x) - \overline{A}\left(\sqrt{k_j}\,\varphi_{k-\langle j\rangle}(x)\right)_{j=1}^{N}$$



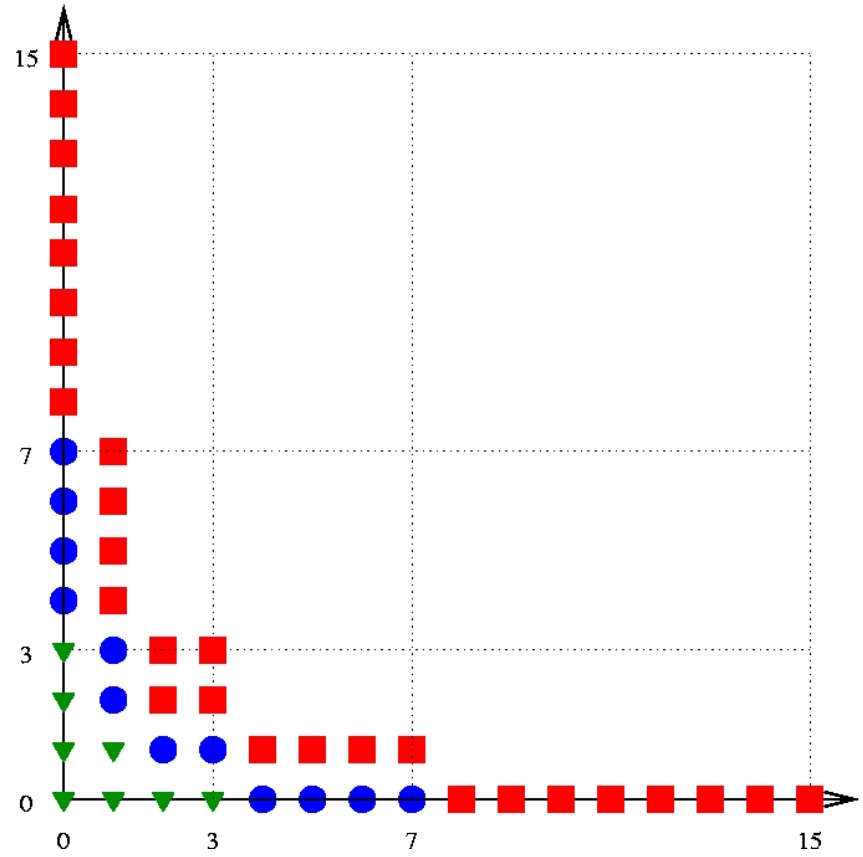


Approximate wavefunction by Hagedorn wavepacket

$$\psi(x,t) \approx e^{iS(t)/\varepsilon} \sum_{k\in\mathcal{K}} c_k(t)\, \varphi_k[q(t),p(t),A(t),B(t)](x)$$

over multi-index set $\mathcal{K}$

- in low dimensions, full cube: $k_j \le K$ $(j = 1,\ldots,N)$
- in moderate dimensions, hyperbolic cross: $(1+k_1)\cdot\ldots\cdot(1+k_N) \le K$
- in high dimensions, axes: $k_j > 0$ only for a single component j in each k (Hartree-type approximation in a moving frame)


15
7
3
0
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7
15

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Bits and pieces

$$H = T + Q_{q(t)} + R_{q(t)}$$

- We can solve exactly the free Schrödinger equation, with the wavefunction remaining in the Hagedorn wavepacket form with unaltered coefficients c_k.
- For a quadratic potential, we can solve exactly the potential equation with the wavefunction remaining in the Hagedorn wavepacket form with the same coefficients c_k.
- For the non-quadratic remainder, we compute the variational approximation of the potential equation on the linear space spanned by the functions φ_k with fixed parameters q, p, A, B, letting the coefficients c_k vary.

Free Schrödinger equation

$$i\varepsilon \frac{\partial \psi}{\partial t} = -\sum_{j=1}^{N} \frac{\varepsilon^2}{2m_j} \frac{\partial^2 \psi}{\partial x_j^2}$$

A time-dependent Hagedorn wavepacket solves the free Schrödinger equation with

$$\begin{aligned} q(t) &= q(0) + t\, M^{-1} p(0) \\ A(t) &= A(0) + t\, M^{-1} B(0) \\ S(t) &= S(0) + t\, \tfrac{1}{2} p(0)^T M^{-1} p(0) \end{aligned}$$

and $p(t) = p(0)$, $B(t) = B(0)$, $c_k(t) = c_k(0)$.
(M =diag(m_j) is the mass matrix.)

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change only position q and A and S

Quadratic potential

$$i\varepsilon \frac{\partial \psi}{\partial t} = Q\psi$$

For a quadratic potential $Q(x)$, a time-dependent Hagedorn wavepacket solves the equation with

$$\begin{aligned} p(t) &= p(0) - t\,\nabla Q(q(0)) \\ B(t) &= B(0) - t\,\nabla^2 Q(q(0))A(0) \\ S(t) &= S(0) - t\,Q(q(0)) \end{aligned}$$

and $q(t) = q(0)$, $A(t) = A(0)$, $c_k(t) = c_k(0)$.

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change only momentum p and B and S

Galerkin approximation for the remainder

$$i\varepsilon \frac{\partial \psi}{\partial t} = R\psi\,, \qquad R = R(x)$$

fix Gauss parameters q, p, A, B in φ_k

Galerkin approximation: $\langle \varphi_k\,,\, i\varepsilon \partial_t u - Ru \rangle = 0 \quad \forall\, k \in \mathcal{K}$
Then:

$$c(t) = \exp\Big(-\frac{it}{\varepsilon}\, F\Big) c(0)$$

with

$$F = (f_{k\ell}), \qquad f_{k\ell} = \langle \varphi_k | R | \varphi_\ell \rangle$$

$F = O(\varepsilon^{3/2})$ if the quadratic Taylor polynomial of R at q vanishes. Therefore, $\exp\big(-\frac{it}{\varepsilon}\, F\big) c(0)$ is computed efficiently using just a few Lanczos iterations with F.

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change only coefficients c_k

Time-stepping algorithm

start from position q^0, momentum p^0, phase S^0,
width matrices A^0, B^0 satisfying the Hagedorn relations

$$A^T B - B^T A = 0\,, \qquad A^* B - B^* A = 2iI\,,$$

and coefficients c_k^0

$$\psi(x, t^0) \approx u^0(x) = e^{iS^0/\varepsilon} \sum_{k \in \mathcal{K}} c_k^0 \, \varphi_k[q^0, p^0, A^0, B^0](x)$$

determine approximation $u^1(x)$ of the same form after time step Δt using a splitting algorithm

Splitting algorithm

1. **Half-step of kinetic part**: updates $q^{1/2}$, $A^{1/2}$, $S^{1/2,-}$.

2. **Full step of potential part**: split the potential

$$V(x) = Q^{1/2}(x) + R^{1/2}(x)$$

   into its quadratic Taylor polynomial $Q^{1/2}(x)$ at $q^{1/2}$ and the remainder

   - solve with quadratic potential $Q^{1/2}$: updates p^1, B^1, $S^{1/2,+}$
   - Galerkin approximation for the non-quadratic remainder $R^{1/2}$: update coefficients c_k^1

3. **Half-step of kinetic part**: updates q^1, A^1, S^1.

Properties

- time-reversible
- preserves the Hagedorn relations of the matrices A and B
- for position q and momentum p: Störmer-Verlet method for the corresponding classical Hamiltonian system
- limit of taking the full basis set φ_k with all $k \in \mathbb{N}^N$: Strang splitting of the Schrödinger equation
- robust in the semi-classical limit $\varepsilon \longrightarrow 0$: approximation in the potential part becomes exact for $\varepsilon \longrightarrow 0$, while the kinetic part is solved exactly for all ε.

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