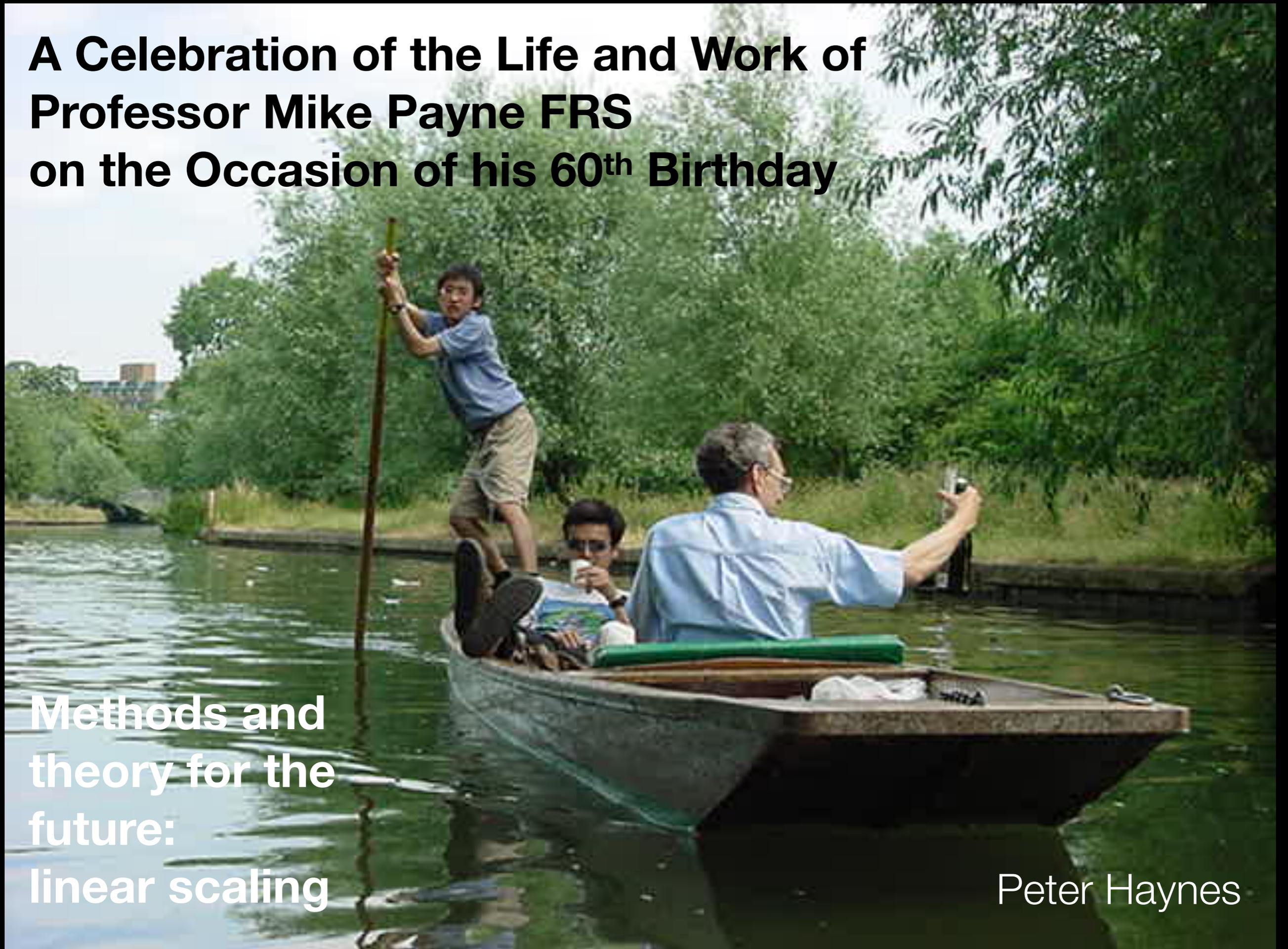


A Celebration of the Life and Work of Professor Mike Payne FRS on the Occasion of his 60th Birthday

Methods and
theory for the
future:
linear scaling

Peter Haynes



QUANTUM PHYSICS II

Michaelmas 1994

M.C. Payne

SYNOPSIS

0. Transitions

- a. Time dependent perturbation theory and Fermi's golden rule.
- b. Spontaneous transitions.
- c. Selection rules.

1. Molecular structure

- a. Born-Oppenheimer approximation.
- b. H_2^+ ion: molecular orbitals, LCAO approximation, g- and u-states.
- c. H_2 molecule; ionic and covalent bonding, correlation, configuration mixing.
- d. Other diatomic molecules, σ - and π -orbitals. Polyatomic molecules, hybridisation.

2. Molecular transitions

- a. Overview: radiative and non-radiative transitions, Raman scattering. Motion of nuclei in Born-Oppenheimer approximation.
- b. Molecular rotation ('symmetric top' molecules only); energy levels, selection rules, spectra, nuclear statistics.
- c. Molecular vibration: energy levels, selection rules: anharmonicity; rotation-vibration bands.
- d. Electronic (vibronic) transitions; Franck-Condon principle; selection rules, band structure, band heads.

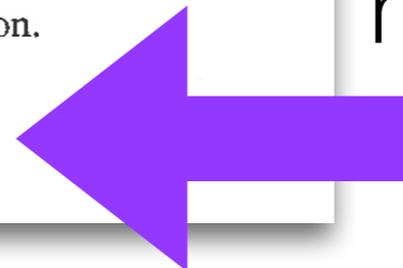
3. Effects of magnetic fields

- a. Particle in uniform magnetic field: vector potential, Larmor precession, Landau levels.
- b. Atomic diamagnetism and paramagnetism; spin, spin-orbit coupling, Lande g-factor.
- c. Zeeman effect: strong and weak fields; selection rules and polarisation.
- d. Magnetic susceptibility; Curie's law.

4. Ab initio quantum mechanical simulations (Non-examinable).

Quantum Physics II
Michaelmas 1994
M.C. Payne

Ab initio quantum
mechanical simulations
(Non-examinable).



Mathematical Physics 3

Dr. M.C. Payne (Room 520, Mott Building), Prof. V. Heine

This course is organised around the 10 $1\frac{1}{2}$ hour examples classes held on tuesdays and fridays from 3pm to 4.30pm starting on 10th February. The lectures cover some but not all of the material covered in the examples classes. The schedule of lectures and examples classes is given below.

	Lectures	Examples classes
3rd February	Lagrangian mechanics and ordinary differential equations	no class
7th February	First order partial differential equations	no class
10th February	Second order partial differential equations	Mechanics
14th February	as above	Ordinary differential equations
17th February	Green's functions, Fourier methods	Partial differential equations
21st February	as above	as above
24th February	Group Theory	Fourier Methods
28th February	as above	as above

Mathematical Physics 3
Spring 1995
M.C. Payne & V. Heine

$$R(r) = r^\ell \quad \text{or} \quad r^{-\ell-1} \quad (5.26)$$

Of the associated Legendre functions, only $P_\ell^m(x)$ for $\ell=0,1,2,\dots$ and $|m|$ an integer less than or equal to ℓ is not infinite at $x = \pm 1$. The first few such functions are

$$P_0^0(\cos\theta) = 1, \quad P_1^0(\cos\theta) = \cos\theta, \quad P_1^1(\cos\theta) = \sin\theta \quad (5.27)$$

The combination $P_\ell^{|m|}(\cos\theta) \exp(im\phi)$ is proportional to the spherical harmonic $Y_{\ell m}(\theta, \phi)$. [Provided m is real P_ℓ^{-m} is proportional to P_ℓ^m].

(iii) Cylindrical coordinates

$$u(x) = P(\rho)\Phi(\phi)Z(z) \quad (5.28)$$

$$\nabla^2 = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \quad (5.29)$$

The separated equations are

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{dP}{d\rho} \right) + (k^2 - \alpha^2 - \frac{m^2}{\rho^2}) P = 0 \quad (5.30)$$

$$\Phi'' = -m^2 \Phi, \quad Z'' = -\alpha^2 Z \quad (5.31)$$

where α and m are constants. With the change of variable $x = \rho\sqrt{k^2 - \alpha^2}$ the equation in ρ becomes Bessel's equation of order m . Thus the solutions are

$$P(\rho) = J_m(\rho\sqrt{k^2 - \alpha^2}) \quad \text{or} \quad Y_m(\rho\sqrt{k^2 - \alpha^2}) \quad (5.32)$$

$$\Phi(\phi) = \exp(\pm im\phi) \quad (5.33)$$

$$Z(z) = \exp(\pm i\alpha z) \quad (5.34)$$

Only $J_m(x)$ with m an integer ≥ 0 is non-singular at $x=0$.

5.3 Eigenfunction expansions

It should be noted that the single variable differential equations obtained by separation of variables in the previous section all take the form of eigenvalue equations for real second order ordinary differential operators. We know that an appropriate choice of weight function $w(x)$ makes such an operator self-adjoint [$\frac{1}{w(x)}Ly = (py) - qy$]. If the boundary conditions in the corresponding variable are also self-adjoint ($|y_j^*py_i|_a = |y_j^*py_i|_b$ for all i,j - which is true for Cauchy, Dirichlet and Neumann boundary conditions) the operator is Hermitian and its eigenfunctions are a complete orthonormal set of functions of that variable. This allows us to find a wide variety of solutions of a PDE in the form of eigenfunction expansions which can be made to converge in the mean to any solution.

Examples (i) Consider the solutions of the wave equation in the interior of the cube with faces $x=0,\pi, y=0,\pi, z=0,\pi$. The separated equations (5.12) involve Hermitian operators if the boundary conditions are chosen to be (for example) $\psi = 0$ on the faces of the cube. The eigenvalues are $m = 1,2,\dots, n = 1,2,\dots, \sqrt{k^2 - m^2 - n^2} = \ell = 1,2,\dots$ with corresponding eigenfunctions

$$X(x) = \sin(mx), \quad Y(y) = \sin(ny), \quad Z(z) = \sin(\ell z) \quad (5.35)$$

Thus any solution of the wave equation may be represented (in the sense of convergence in the mean) in the interior of the cube by an eigenfunction expansion

$$\psi(x,t) \stackrel{*}{=} \sum_{\ell m n} \sin(mx)\sin(ny)\sin(\ell z) [a_{\ell m n}^+ \exp(ict\sqrt{\ell^2+m^2+n^2}) - a_{\ell m n}^- \exp(-ict\sqrt{\ell^2+m^2+n^2})] \quad (5.36)$$

where $\stackrel{*}{=}$ means 'equals in the sense of convergence in the mean'. If ψ vanishes on the faces of the cube the expansion actually converges uniformly to ψ throughout the cube. The individual terms in the expansion are called the normal modes of oscillation of the cube. The

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Photo 13



“Why don’t you see if there’s anything in these order- N methods?”

– MCP, 2 October 1995

First Year Report 12 June 1996

1 Introduction

First Year Report
12 June 1996

Linear Scaling Total Energy Pseudopotential Calculations for Large Systems

Peter Haynes
Christ's College

Supervisor: Dr. M. C. Payne

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, U.K.

Much interest has recently been shown in developing methods to perform *ab initio* total energy pseudopotential calculations within density functional theory (DFT) in which both the computational effort and memory required scale linearly with the system size (so-called $O(N)$ methods.) One approach involves minimisation of an energy functional with respect to the single-particle density matrix, and here this is developed from the conventional formulation of DFT. This method is implemented by discretising the wave functions and Hamiltonian on a real-space grid. A method is also presented for obtaining an initial estimate of the density matrix from conventional $O(N^3)$ calculations and the results compared with the best estimate obtained from an LCAO approach. Finally, a new implementation of the method which is currently being developed is described, which has several advantages over the real-space grid method and is much closer to traditional plane-wave methods.

“a new implementation of the method ... is described, which ... is much closer to traditional plane-wave methods”

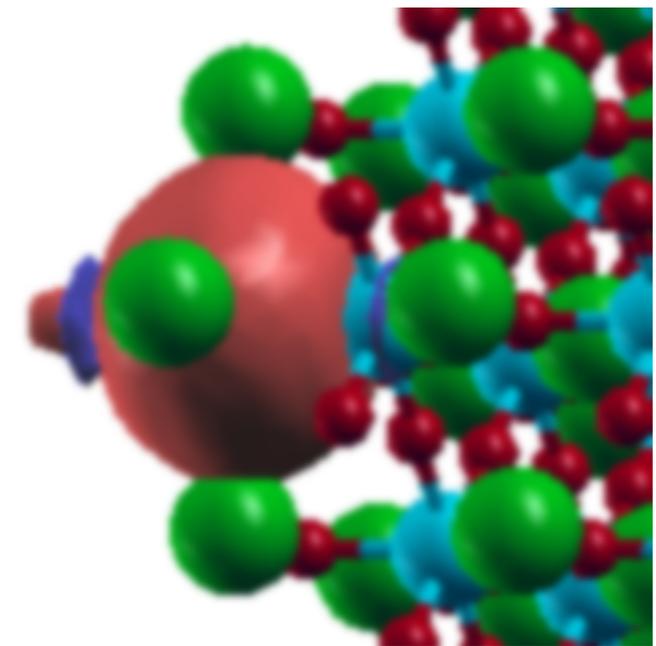
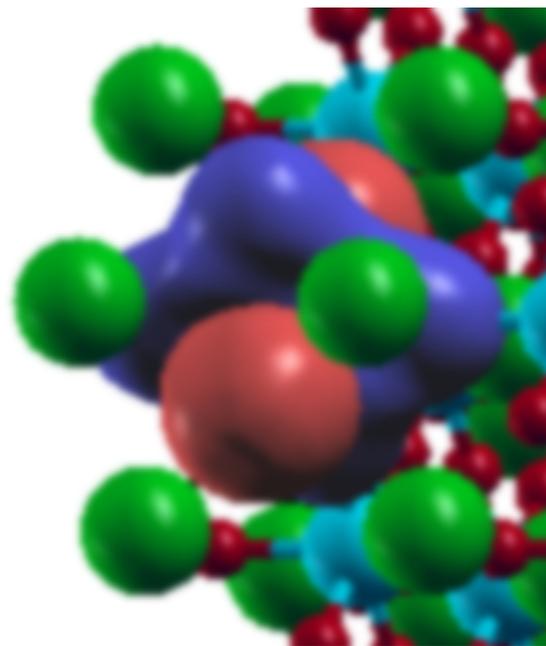
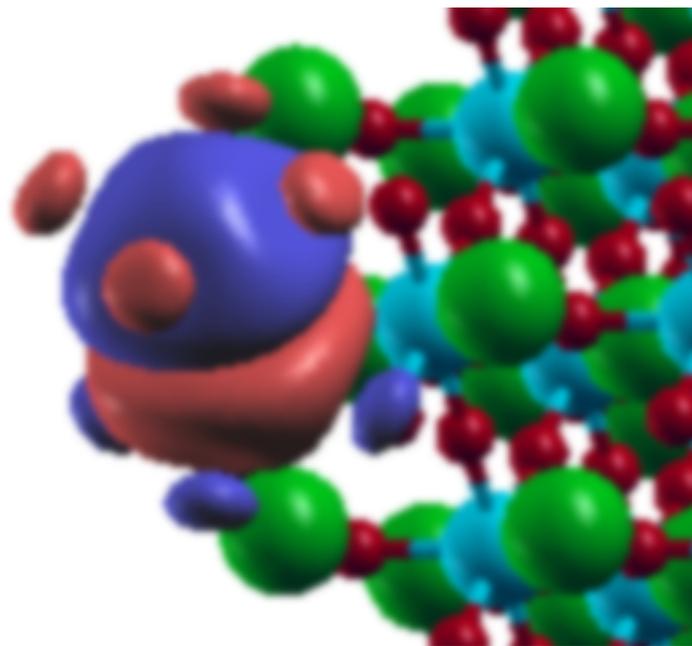


Image credit: Harvard University Archives

diagonal in
momentum
space

$$\nabla^2 \phi_\alpha$$

localised in
real space



4.1.1 Kinetic energy

The action of the Laplacian operator on the support functions can be calculated using a finite difference technique. For a function $f(x)$ defined on a grid of spacing h , the second derivative to second order in the grid spacing is

$$\frac{d^2 f}{dx^2}(n_x) \simeq \frac{-f(n_x - 2) + 16f(n_x - 1) - 30f(n_x) + 16f(n_x + 1) - f(n_x + 2)}{12h^2} \quad (40)$$

where n_x labels the grid point. This expression can be used to calculate $\partial^2 \phi_\alpha / \partial x^2$, $\partial^2 \phi_\alpha / \partial y^2$, $\partial^2 \phi_\alpha / \partial z^2$ and therefore $\nabla^2 \phi_\alpha$ approximately at each point. The kinetic energy is then given by

$$E_K = 2 \sum_{\alpha\beta} K_{\alpha\beta} T_{\beta\alpha} \quad (41)$$

where

$$T_{\beta\alpha} = -\frac{1}{2} \int d^3 r \phi_\beta(\mathbf{r}) \nabla_{\mathbf{r}}^2 \phi_\alpha(\mathbf{r}) \quad (42)$$

and the integral is calculated by summing over grid points as for $S_{\alpha\beta}$. We have also calculated the kinetic energy by Fourier transforming each support function and then operating with the Laplacian, which is diagonal in reciprocal-space:

$$\nabla_{\mathbf{r}}^2 \phi_\alpha(\mathbf{r}) = \mathcal{F}^{-1} \left(-q^2 \tilde{\phi}_\alpha(\mathbf{q}) \right) \quad (43)$$

where \mathcal{F}^{-1} denotes taking the inverse Fourier transform. The matrix elements $T_{\alpha\beta}$ are then calculated by summing over grid points as before. The discrete Fourier transform is calculated using a fast Fourier transform (FFT) applied to the smallest rectangular grid which encloses the spherical support region.

Localised basis functions

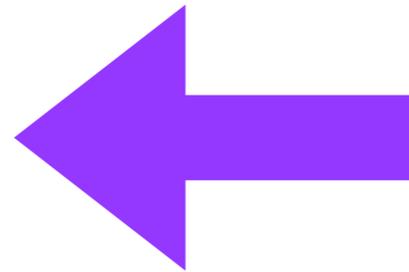
- Plane-waves efficiently describe systems with a weak potential and obey the free-particle Schrödinger (Helmholtz) equation:

$$(\nabla^2 + k^2) \xi(\mathbf{r}) = 0$$

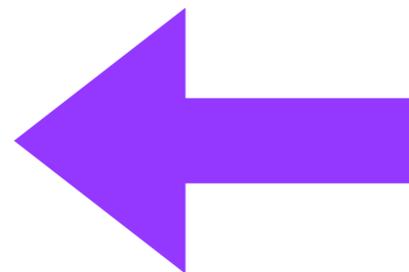
where the kinetic energy of the plane-wave is $E = \frac{1}{2}k^2$

- Appropriate boundary conditions for the support functions and hence the basis functions which describe them are that the functions vanish at the surface of the support regions.
- The solution to the Helmholtz equation with these boundary conditions for a sphere of radius R centred at the origin is:

$$\xi(\mathbf{r}) = \begin{cases} \sum_{nlm} c_{nlm} j_l(k_{nl}r) Y_{lm}(\vartheta, \varphi) & r \leq R \\ 0 & r > R \end{cases}$$

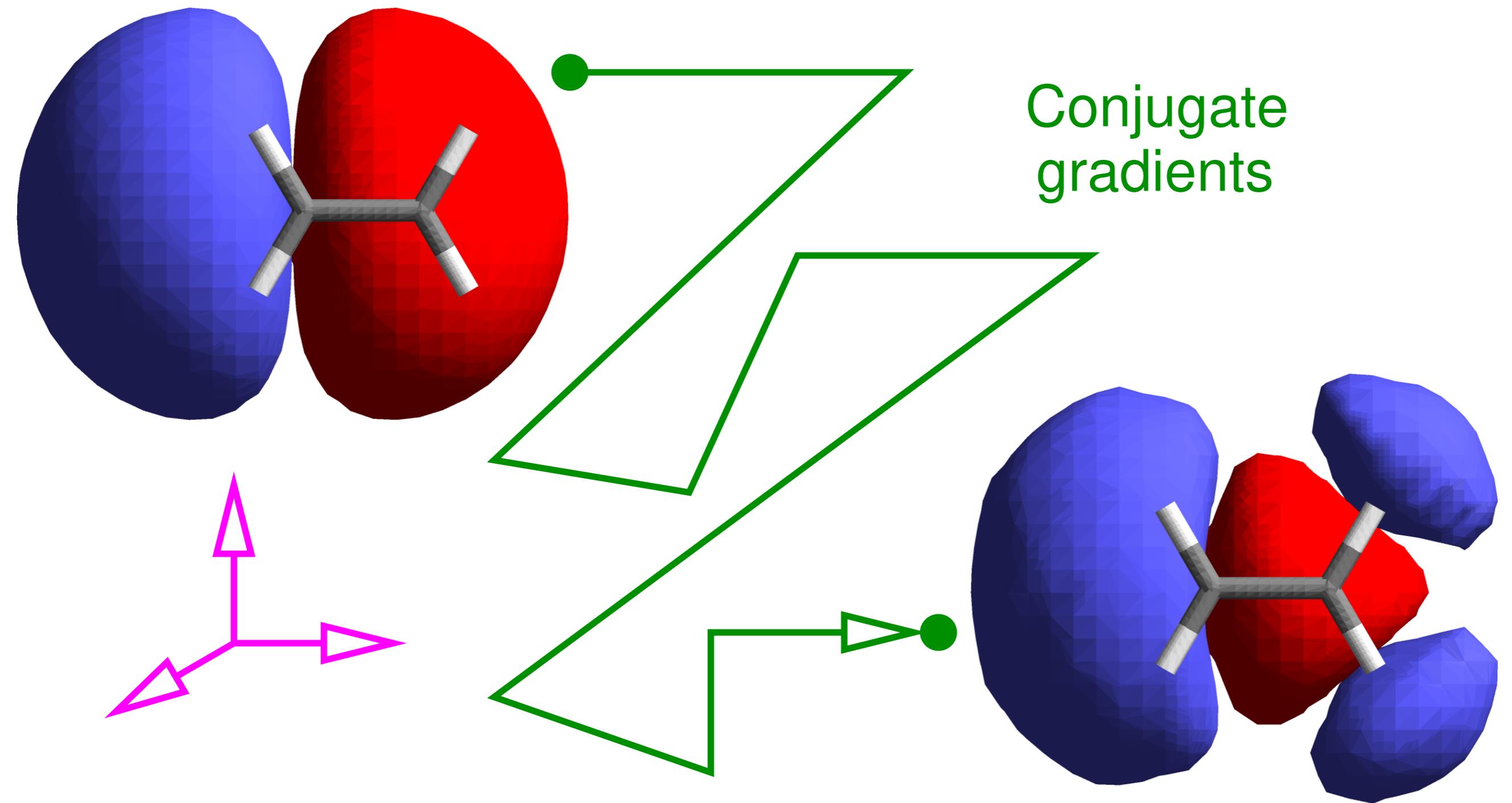


same equation



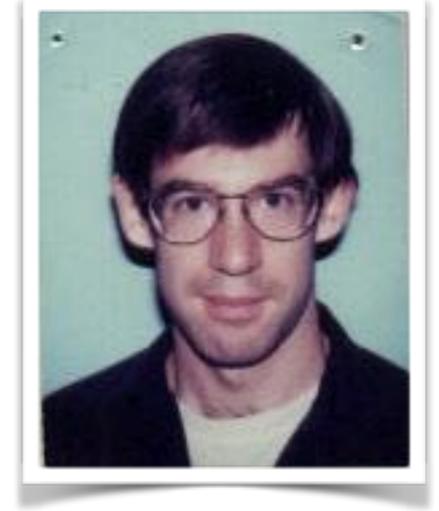
different boundary conditions

Advantages of orthogonal basis sets



$$\hat{P} = 1 - |v\rangle\langle v| = 1 - \sum_{\alpha\beta} v_{\alpha} |\chi_{\alpha}\rangle S_{\alpha\beta}^{-1} \langle\chi_{\beta}| v_{\beta}$$

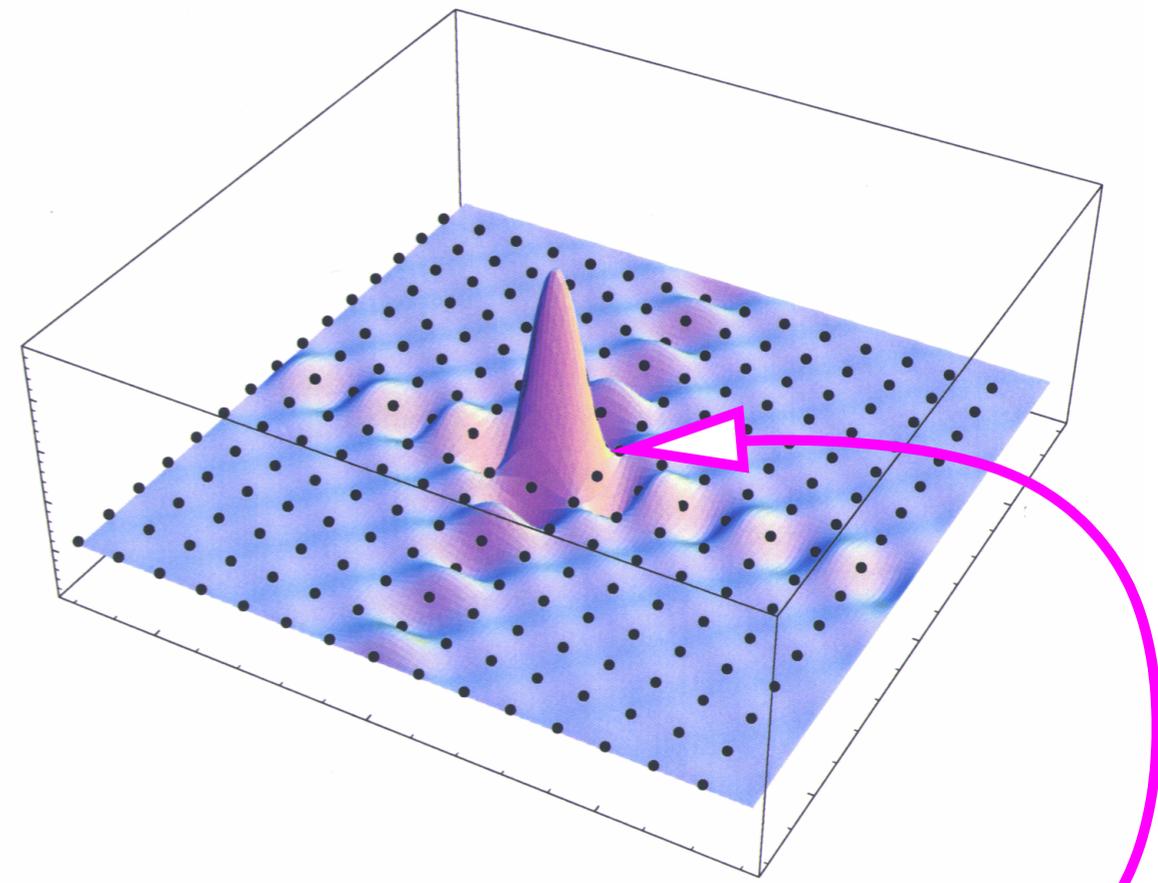
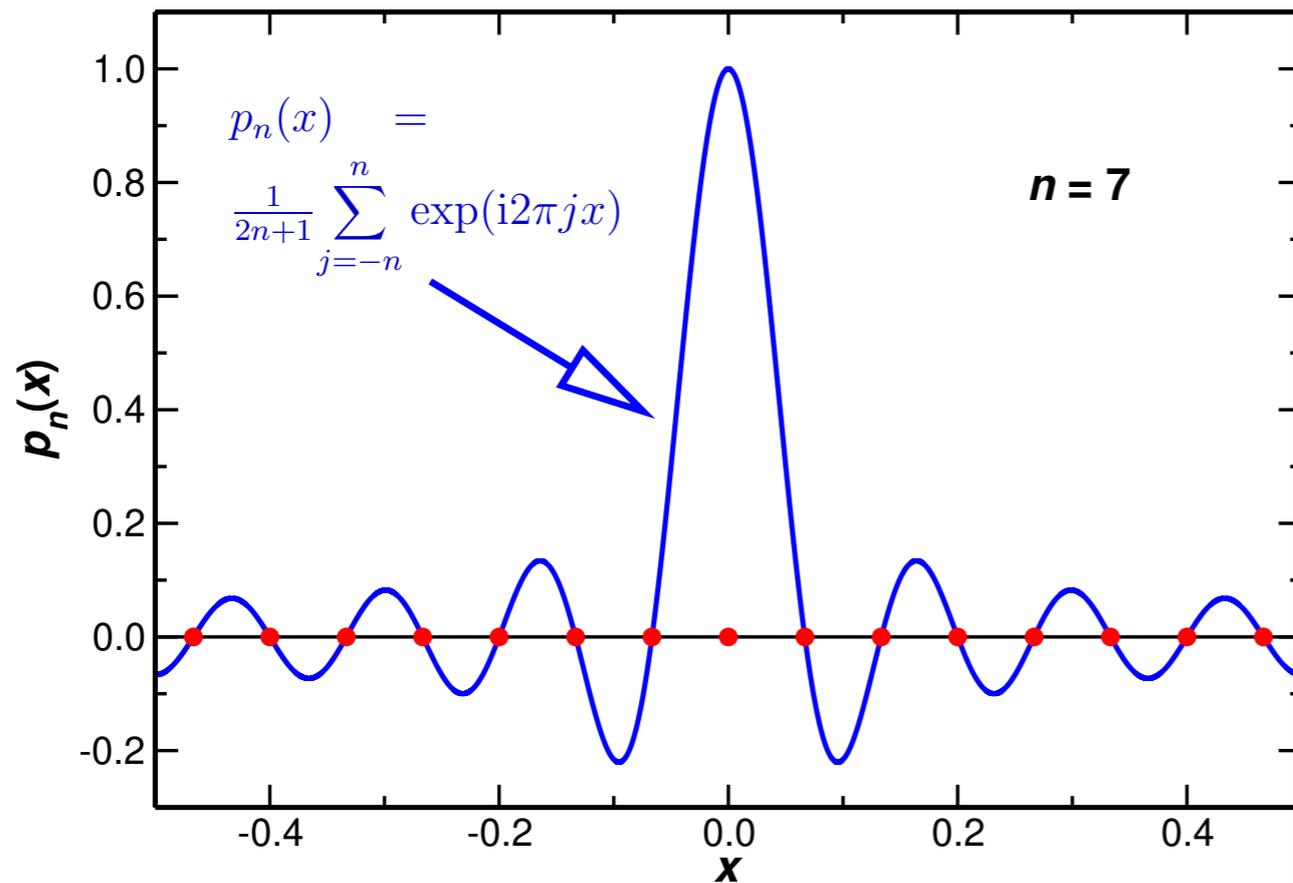
ONETEP Developers then



ONETEP Developers today



PSINC Orthogonal Basis Set (Periodic Cardinal Sine)

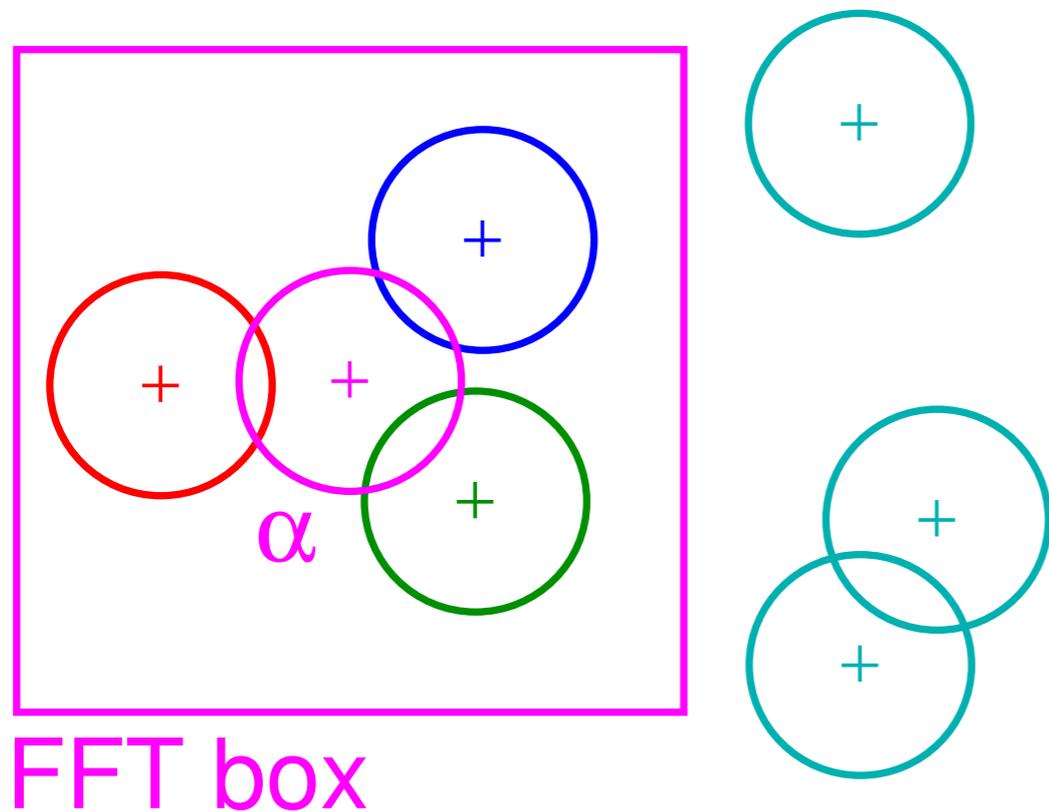


Define a basis set of 3D PSINC's on a regular grid \mathbf{r}_{ijk} :

$$D_{ijk}(\mathbf{r}) = p_{n_1} \left(\frac{x}{a_1} - \frac{i}{2n_1+1} \right) p_{n_2} \left(\frac{y}{a_2} - \frac{j}{2n_2+1} \right) p_{n_3} \left(\frac{z}{a_3} - \frac{k}{2n_3+1} \right)$$

- Real linear combinations of plane-waves
- Localized: $D_{ijk}(\mathbf{r}_{lmn}) = \delta_{il} \delta_{jm} \delta_{kn}$
- Orthogonal: $\int D_{ijk}(\mathbf{r}) D_{lmn}(\mathbf{r}) d^3r = w \delta_{il} \delta_{jm} \delta_{kn}$

FFT box technique – introduction



- Define a box for each function $\phi_{\alpha}(\mathbf{r})$
 - centred on that function
 - universal shape and size
- Apply fast Fourier transforms in this box
 - to generate the charge density
 - to apply all terms in the Hamiltonian
- This method guarantees
 - consistent action of the Hamiltonian
 - Hermitian Hamiltonian matrix
 - linear scaling cost per iteration

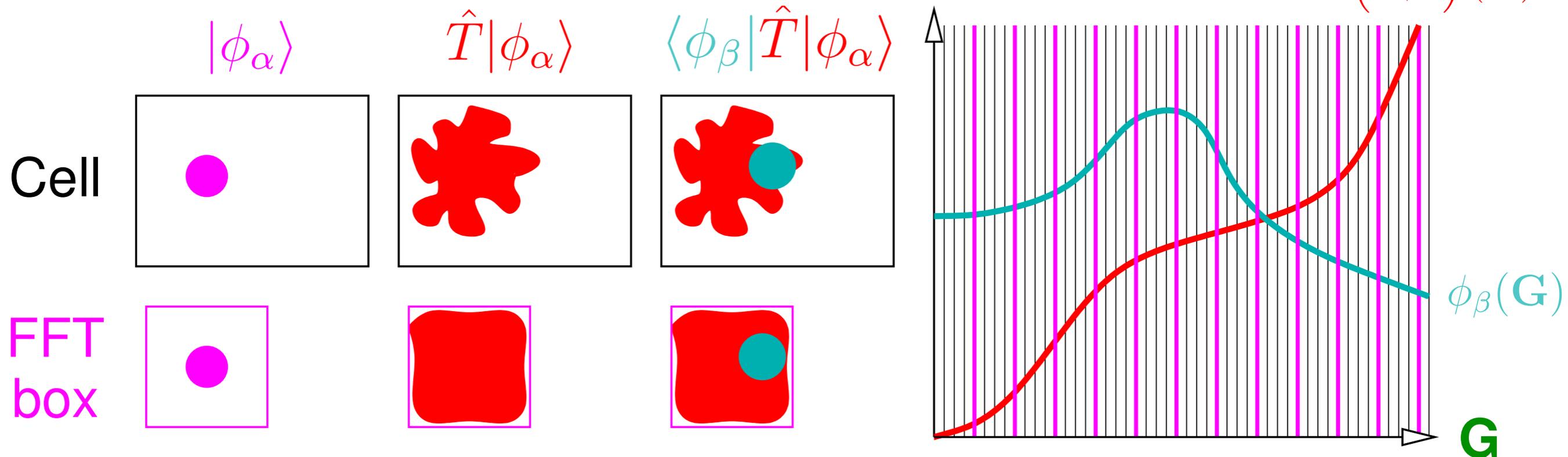
FFT box technique – justification

- Define a set of PSINC's for the FFT box: $d_{ijk}^\alpha(\mathbf{r})$
- Transfer functions from the cell to the FFT box using projection operators

$$\hat{P}_\alpha = \sum_{\mathbf{r}_{ijk} \in \text{box } \alpha} |d_{ijk}^\alpha\rangle \langle D_{ijk}|$$

- Replaces $\hat{H}|\phi_\alpha\rangle$ by $\hat{P}_\alpha^\dagger \hat{H} \hat{P}_\alpha |\phi_\alpha\rangle$

Equivalent to a coarse sampling in momentum–space: $(\hat{T}\phi_\alpha)(\mathbf{G})$





ONETEP

Original aims
stated in
Accelrys
presentation in
2004:

- True linear scaling
 - ✦ computational time
 - ✦ resources e.g. memory
- Controlled accuracy
 - ✦ minimal to systematic basis set
 - ✦ impose “nearsightedness”
- Parallel scalability
- Robust reliability
- General purpose
 - ✦ molecules, surfaces, solids
 - ✦ insulators, metals?

MIKE PAYNE

Happy birthday Mike!

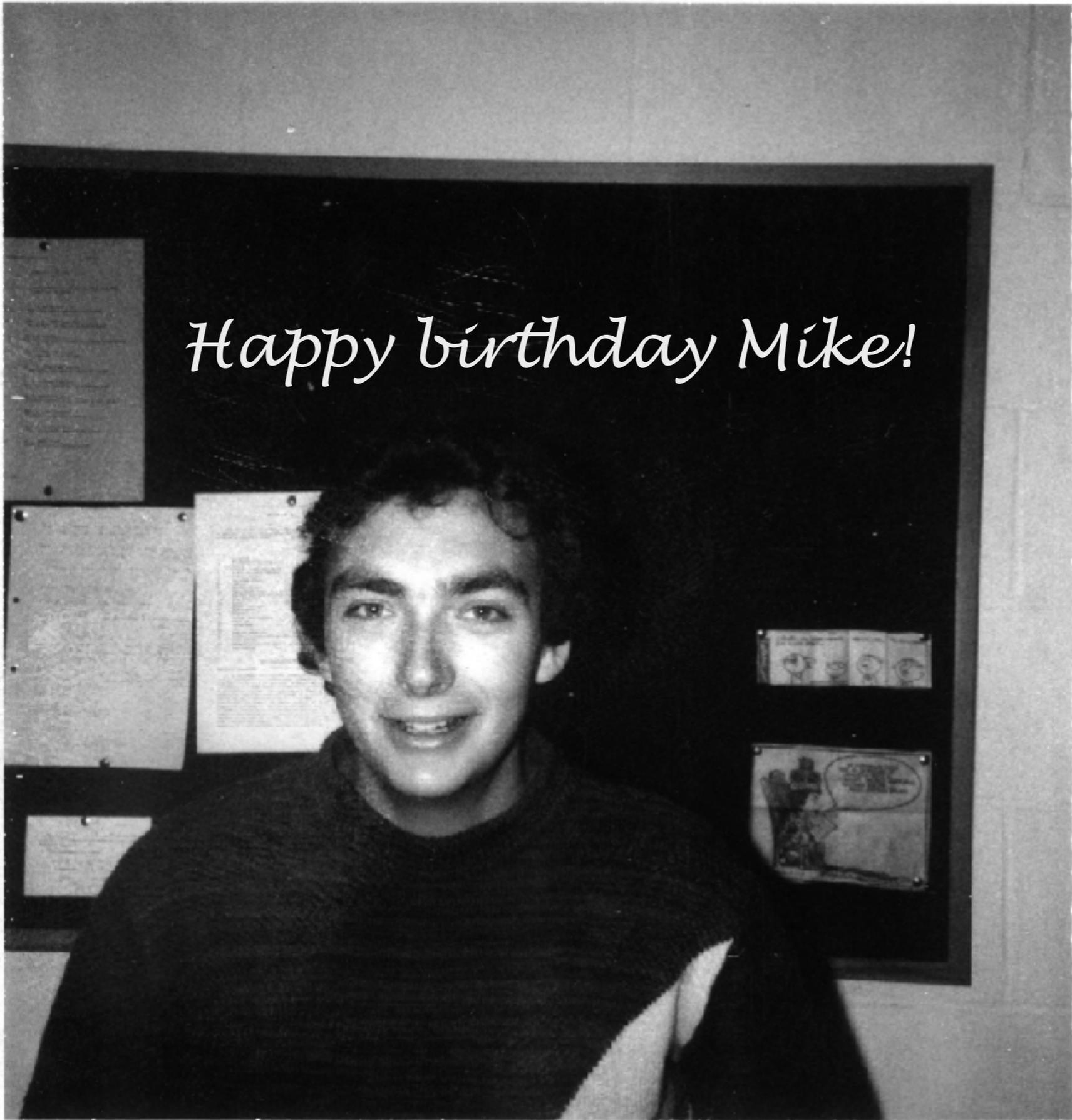


Image credit: Cavendish Laboratory