Electronic structure Periodic boundary conditions TCM 1993-6

Mike Payne's 60th Birthday – Celebratory symposium

Guy Makov, Ben-Gurion University

Beginnings 1993

Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients

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This article describes recent technical developments that have made the total-energy pseudopotential the most powerful ab initio quantum-mechanical modeling method presently available. In addition to present ing technical details of the pseudopotential method, the article aims to heighten awareness of the capabilities of the method in order to stimulate its application to as wide a range of problems in as many scientific

I. Introduction II. Total-Barrey Pseudopotential Calculations III. Total-Barrey Pseudopotential Calculations III. Total-Barrey Pseudopotential Calculations III. Total-Barrey Pseudopotential Calculations III. Constructions III. Computational procedure with mol Department of a process of a pr	
I. Introduction I. Total-Energy Pendopotential Calculations A. Overview of approximations II. Total-Energy Pendopotential Calculations III. Total-Energy Pendopotential Calculations III. Total-Energy Pendopotential Calculations III. Total-Energy Pendopotential Calculations III. Computational procedure with mol Interpolation III. Computational procedure with mol Interpolation III. Interpolation III. Interpolation III. Interpolation III. Interpolation III. Calculation of charge density on III. Calculation of Arage density III. Calculation of Pendre III. Calculation of Pendre III. Calculation of Pendre III. Interpolation III. Interpolat	1062
II. Total-Energy Pseudopotential Calculations 1049 1. Computational procedure with mol 6. Deciro deproximations 1049 1. Instabilities and fluctuations in the 1049 1. Instabilities and fluctuations in the 1050 1. Exchange and correlation 1050 1. Computational cost of molecular dy 1050 1. Calculation of charge density 1051 1. Calculation of charge density 1052 1. Calculat	1062
A. Overview of approximations 1049 B. Electron-electron interactions 1050 1. Exchange and correlation 2. Density-functional theory 3. The Kohn-Sham energy functional 3. Robert Sham energy functional 3. Robert Sham energy functional 3. Robert Sham energy functional 3. Representation of the coefficients 4. Integration of equations of notice of the coefficients 4. Integration of equations of most of the coefficients 5. Orthogonalization 6. Comparison to conventional nutries 6. Comparison to conventional nutries 7. Plane-wave Posts sets 7. Plane-wave persentation of Kohn-Sham equations 8. Norm conservation 1054 1. Preudopotential approximation 1054 1. Norm conservation 1055 2. Convergence properties 1056 3. Functure factor 1056 4. Plane-wave basis sets 1056 5. Structure factor 1057 6. Comparison of wave function 1058 6. Convergence properties 1059 6. Orthogonalization of wave function 1050 6. Convergence properties 1056 6. Comparison between algorithms 1. The Crams-Schmidt scheme 1057 6. Comparison between algorithms 1. The Crams-Schmidt scheme 1058 6. Comparison between algorithms 1. Integration of wave function 1. The Crams-Schmidt scheme 1059 1. The Crams-Schmidt scheme 1050 1. The Crams-Schmidt scheme 1051 1. The Crams-Schmidt scheme 1052 1. The Crams-Schmidt scheme 1053 1. The Crams-Schmidt scheme 1054 1. The Crams-Schmidt scheme 1055 1. The Crams-Schmidt scheme 1056 1. Comparison between algorithms 1. The Crams-Schmidt scheme 1. The Crams-Schmidt s	1063
A. Overview of approximations 1049 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations of most 1. Instabilities and fluctuations of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations 1. Instabilities and fluctuations in the ergy 1. Calcal pendicts of the coefficients 1. Instabilities and fluctuations in the ergy 1. Instabilities and fluctuations 1. Instabilities and fluctuations 1. Instabilities and fluctuations 1. Instabilities and fluctuations 1. Instab	ecular dynamics 106:
B. Electron-electron interactions 1050 ergy 1. Exchange and correlation 1050 (S. Computational cost of molecular dy 2. Density-functional theory 1050 (S. Computational cost of molecular dy 3. The Kohn-Sham energy functional 1050 (S. Construction of Hamiltonian molecular dy 4. Local-ensity approximation 1051 (S. Periodic supercells 1051 (S. Orthogonalization of equations of molecular dy 5. September 1052 (S. Computation of countries of the conflicients of the coefficients of the coe	Kohn-Sham en-
1. Exchange and correlation 1050 K. Computational cost of molecular dy 2. Density/mictional theory 1050 C. Alculation of charge density 1050 C. Construction of Hamiltonian ms 1050 C. Construction of Hamiltonian ms 1050 C. Construction of Hamiltonian ms 1051 C. Local-density approximation 1051 C. Local-density approximation 1051 C. Local-density approximation 1051 C. Construction of equations of notification 1051 C. Construction of equations of most 1052 C. Construction of equations of most 1052 C. Construction of Execution 1052 C. Construction of Execution 1053 C. Construction interactions 1054 C. Construction interactions 1054 C. Construction of wave function 1055 C. Construction of wave function 1055 C. Construction of wave function 1056 C. Convergence properties 1056 C. Convergence to Koha-Sham eight 1056 C. Construction 1056 C. Constructi	1063
2. Density-functional theory 1050 1. Calculation of charge density a. The Kohn-Sham energy functional 1050 2. Construction of Hamiltonian man b. Kohn-Sham enguations 1051 3. Accelerations of the coefficients C. Periodic supercells 1051 5. Orthogonalization 1. Block's theorem 1052 6. Comparison to conventional man 2. A plane wave basis sets 1052 17. Local pseudopotentials 3. Nonperiodic systems 1053 1. Analytic integration of second-of motion interactions interactions 1054 1. Plane-wave basis sets 1055 1. Analytic integration of second-of motion of motion 2. Convergence properties 1055 6. Orthogonalization of wave function of motion of	namics 1064
a. The Kohn-Sham energy functional 1050 2. Construction of Hamiltonian ms 1050 3. Accelerations of the coefficients of the coe	106
b. Kohn-Sham equations c. Local-fessity approximation Districtions of the coefficients c. Cerefroidic supercells 1051 C. Periodic supercells 1051 C. Periodic supercells 1052 C. kepoint sampling 1052 C. kepoint sampling 1053 C. Planc-wave basis sets 1053 C. Nonperiodic systems 1053 D. Electro-in interactions 1054 C. Planc-wave perocedure 1055 D. Generation procedure 1055 D. Generation procedure 1056 D. Forthogonalization of evacuations 1057 Local pasedopotential approximation 1054 C. Normy conservation 1054 C. Normy conservation 1055 D. Generation procedure 1055 D. Generation procedure 1056 D. Orthogonalization of evacuations 1057 D. Local pasedopotentials 117. Improvements in Algorithms 1054 Of motion 1056 D. Orthogonalization of evacuations 1057 D. A lampoved integration of second-of motion 1056 D. Orthogonalization of conventional material integration of second-of motion 1057 D. Hortogeneuric properties 1057 D. Orthogonalization of evacuations 1058 D. A lampoved integration of second-of motion 1058 D. Orthogonalization of conventional material integration of second-of motion 1058 D. Integration of second-of motion 1058 D. Orthogonalization of evacuations 1058 D. Improvements in Algorithms 1058 D. A limprovements in Algorithms	atrix 106
C. Perfodic supercelli 1. Block's theorem 1051 2. kepoint sampling 1052 3. Plane-wave basis sets 1052 4. Plane-wave basis sets 1053 5. Nonperfodic systems 1053 5. Nonperfodic systems 1054 1. Peudopotential approximation 1054 1. Peudopotential approximation 1054 1. Peudopotential approximation 1054 1. Peudopotential approximation 1055 1. Generation procedure 1055 1. Generation procedure 1055 1. The Grams-Schmidt scheme 1056 1. The Grams-Schmidt scheme 1056 1. The Grams-Schmidt scheme 1056 2. Convergence to Koha-Sham eige 1056 2. Convergence to Koha-Sham eige 1056 2. Convergence and porture factor 1056 2. Convergence to Koha-Sham eige	106
C. Periodic supercelli 1. Bloch's theorem 1051 2. k-point sampling 1052 3. Plane-wave basis sets 1053 4. Plane-wave basis sets 1053 5. Nonperiodic systems 1053 5. Nonperiodic systems 1054 1. Petudopotential approximation 1054 1. Petudopotential approximation 1054 1. Petudopotential approximation 1054 1. Petudopotential approximation 1055 1056 1057 1058 1059 1059 1059 1059 1059 1059 1059 1059	on 106:
1. Bloch's theorem 1052 6. Comparison to conventional materials with the comparison of Conventional materials of the Comparison to Conventional materials of the Comparison to Conventional materials of the Comparison to Conventional of Comparison to Conventional of Comparison theorem 1053 1. Improvements in Algorithms 1053 1. Analytic integration of Second-on 1054 1. Analytic integration of Second-on 1055 1. Analytic integration of First-order motion 1055 1. Convergence properties 1055 1. The Grans-Schmidt scheme 1056 1. The Grans-Schmidt scheme 1056 1. The Grans-Schmidt scheme 1056 1. Convergence to Kohn-Sham eight 1056 1. Comparison between algorithms 1056 1. Comparison between algorithms 1056 1.	106
2. Spinor wave basis sets 1052 2. Plane-wave basis sets 1052 3. Plane-wave basis sets 1053 4. Plane-wave persentation of Kohn-Sham equations 1053 5. Electro-ion interactions 1054 6. Plane-wave persentation 1054 6. Plane-wave basis sets 1056 6. Plane-wave basis sets 1056 6. Structure factor 1055 C. Convergence properties 1055 C. Structure factor 1056 C. Convergence properties 1056 C. Structure factor 1056 C. Comparison between algorithms	trix diagonaliza-
3. Plane-wave basis sets . 1052 7. Local pseudopotentials . 1052 1. Plane-wave basis sets . 1053 2. Nonperiodic systems . 1053 1. Pseudopotential approximation . 1054 2. Nonperiodic systems . 1055 1. Pseudopotential approximation . 1054 2. Norm conservation . 1055 1. Pseudopotential approximation . 1055 1. The Grama-Schmidt scheme . 1056 1. The Grama-Schmidt scheme . 1056 1. The Grama-Schmidt scheme . 1056 1. Convergence to Kohn-Sham eight . 1056 1. Comparison between algorithms . 1056 1. Comparison between algorithms . 1056 1. The Grama-Schmidt scheme . 1056 1. Comparison between algorithms . 1056 1. The Grama-Schmidt scheme . 1056 1. Comparison between algorithms . 1056 1. The Grama-Schmidt scheme . 1056 1. Comparison between algorithms . 1056 1. The Grama-Schmidt scheme . 1056 1. The Grama-Sc	106
tions 1053 A. Improved integration 1055 Nonperiodic systems 1053 1. Analytic integration of second-o of motion 1. Pseudopotential approximation 1054 0. Freedopotential approximation 1055 motion 1055 0. Generation procedure 1055 B. Orthogonalization of wave function 1056 0. Convergence properties 1056 1. The Grama-Schmidt scheme 1056 0. Structure factor 1056 0. Convergence to Kohnsham eight 1056 0. Comparison between algorithms 1056 0. Comparison between algorithms 1056 0.	106
tions 1033 A. Improved integration 2 S. Nonperiodic systems 1033 I. Analytic integration of second-order of the control of th	106
D. Electron-ion interactions 1054 of motion 1. Pseudoportatial approximation 1054 2. Analytic integration of first-orde motion a. Norm conservation 1055 motion b. Generation procedure 1055 B. Orthogonalization of wave function c. Convergence properties 1056 1. The Grams-Schmidt scheme d. Plane wave basis sets 1056 2. Convergence to Kohn-Sham eigs 2. Structure factor 1056 C. Comparison between algorithms	106
D. Electron-ion interactions 1054 of motion 1. Pseudoportatial approximation 1054 2. Analytic integration of first-orde motion a. Norm conservation 1055 motion b. Generation procedure 1055 B. Orthogonalization of wave function c. Convergence properties 1056 1. The Grams-Schmidt scheme d. Plane wave basis sets 1056 2. Convergence to Kohn-Sham eigs 2. Structure factor 1056 C. Comparison between algorithms	rder equations
1. Pseudopotential approximation 1054 2. Analytic integration of first-orde motion 1055 b. Generation procedure 1055 b. Orthogonalization of wave function c. Convergence properties 1056 l. The Grams-Schmidt scheme d. Plane-wave basis sets 1056 c. Convergence to Kohn-Sham eige 2. Streuture factor 1056 c. Comparison between algorithms	1067
a. Norm conservation 1055 motion b. Generation procedure 1055 B. Orthogonalization of wave function c. Convergence properties 1056 1. The Gram-Schmidt scheme d. Plane wave basis sets 1056 2. Convergence to Kohn-Sham eige 2. Structure factor 1056 C. Comparison between algorithms	r equations of
b. Generation procedure 1055 B. Orthogonalization of wave function c. Convergence properties 1056 1. The Gram-Schmidt scheme d. Plane-wave basis sets 1056 2. Convergence to Kohn-Sham eige 2. Structure factor 1056 C. Comparison between algorithm of the control o	1068
d. Plane-wave basis sets 1056 2. Convergence to Kohn-Sham eige 2. Structure factor 1056 C. Comparison between algorithms	
d. Plane-wave basis sets 1056 2. Convergence to Kohn-Sham eige 2. Structure factor 1056 C. Comparison between algorithms	1068
 Structure factor Structure factor C. Comparison between algorithms 	
	1065
	1065
E. Ion-ion interactions 1057	
F. Computational procedure with conventional matrix V. Direct Minimization of the Kohn-Sham	
diagonalization 1057 tional	1069
G. Drawbacks of conventional procedure 1058 A. Minimization of a function	1070
H. Alternative methods 1058 1. The method of steepest descents	1070
II. The Molecular-Dynamics Method 1058 2. The conjugate-gradients techniques	ue 1070
A. Eigenvalue solution by successive "improvement" of B. Application of the conjugate-gradier	nts method 1072
a trial wave function 1058 1. The update of a single band	1072
B. Molecular-dynamics procedure 1059 2. Constraints	1072
1. Molecular-dynamics Lagrangian 1059 3. Preconditioning	1072
2. Constraints 1059 4. Conjugate directions	1074
C. Molecular-dynamics equations of motion 1060 5. Search for the energy minimum	1074
1. Unconstrained equations of motion 1060 6. Calculational procedure	1075
2. Constrained equations of motion 1060 7. Computational cost	1076
3. Partially constrained equations of motion 1060 C. Speed of convergence	1076
D. Integration of equations of motion 1061 1. Large energy cutoff	1076
1. The Verlet algorithm 1061 2. Long supercells	1077
Stability of the Verlet algorithm 1061 3. A real system	1077

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• The "agenda":

Expanding application of Total Energy methods

Condensed matter

Materials Science

Chemistry

Biochemistry

• • • •

Cluster project

- Obtain the relaxed cluster structures of (Nb)n
- Calculate the IP as a function of size
- Relaxation of ionic positions

Cluster project

- Obtain the relaxed cluster structures of (Nb)n
- Calculate the IP as a function of size
- Relaxation of ionic positions

- Computational resources
 - Cray
 - Workstations
- Convergence of supercells

The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method

M Leslie† and M J Gillan‡

JPhysC (1985)

- "However, what we want is not this energy Earray in a periodic array of defects, but the energy E of a defect in an otherwise perfect infinite crystal."
- "It seems likely that the dominant correction will be due to the Coulomb interaction between the defects."
- "If the repeating unit is large, we can treat this by a macroscopic approximation, ... the Coulomb energy of a periodic array of point charges Q with a neutralising background immersed in a structureless dielectric."

$$\Delta E = \Delta E_{\rm array} + \frac{1}{2}\alpha Q^2/\varepsilon_0 L .$$

Problem formulation

$$\phi(\mathbf{r}) = \int_{\text{sample}} d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$= \sum_{l} \int_{\text{cell}} d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}' + l|} , \qquad (2)$$

Electrostatics only

Fixed density – isolated defect

Periodic boundary conditions in ab initio calculations

G. Makov and M. C. Payne

- Results for atoms/molecules/clusters
 - Neutral systems converge as O(L⁻⁵)
 - Charged or dipolar can converge as rapidly
- Results for condensed matter e.g. charged point defects
 - Could converge as O(L⁻⁵) with effective quantities dielectric constant, quadrupole moment

Publication

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THE PHISIOAL MEYER 049 PHYSICAL REVIEW LETTERS Internet: pra, prb, prc, prd, pre, or pri@aps.org 7 November 1994 Dr. G. Makov Dept. of Physics, TCM Group Cavendish Laboratory University of Cambridge Madingley Road Cambridge CB3 0HE, ENGLAND Re: BU5270 Periodic boundary conditions in ab By: G. Makov and M.C. Payne Dear Dr. Makov: We are pleased to inform you that the above manuscript has been accepted for publication as a regular article in Physical Review B. Please note the publication charge information below and return the attached form indicating 'acceptance' or 'nonacceptance' as soon as possible. Yours sincerely, Partito Berla An Peter D. Adams Physical Review B The current publication charge is \$50 per printed page plus \$50 per article in support of publication of the abstract in Physical Review Abstracts. The entimated charge for your manuscript is \$550 which includes the \$50 abstract charge: the final charge based on the actual number of printed pages may differ. PLEASE NOTE: Reprints must be billed and shipped to a single address.

Impacts

- First citation (1995)
- 1996
 - Resta Theory of polarization in PBC
 - Car Application to molecules, clusters, defects
 - Payne PBC, Applications
 - Needs PBC for QMC
- Improvements, testing, exceptions, application, citation,...

Periodic boundary conditions in *ab initio* calculations. II. Brillouin-zone sampling for aperiodic systems

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 How to sample k-points to accelerate convergence of aperiodic systems due to defect band dispersion?

Periodic boundary conditions in *ab initio* calculations. II. Brillouin-zone sampling for aperiodic systems

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 How to sample k-points to accelerate convergence of aperiodic systems due to defect band dispersion?

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First-principles calculations for point defects in solids

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TCM memories

