A Mixed Basis Approach for the Efficient Calculation of Potential Energy Surfaces

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Abstract

First principles calculations based on density functional theory are having an increasing impact on our understanding of molecule–surface interactions. For example, calculations of the multi-dimensional potential energy surface have provided considerable insight into the dynamics of dissociation processes. However, these calculations using a plane-wave basis set are very compute expensive if they are to be fully converged with respect to the plane-wave energy cutoff, k–point sampling, supercell size, slab thickness, etc. Because of this, in this study, we have implemented a mixed-basis approach which uses pseudo-atomic orbitals and a few low-energy plane waves as the basis set within a density functional, pseudopotential calculation. We show that the method offers a computationally cheap but accurate alternative. The energy barrier for hydrogen dissociation on Cu(111) is calculated as an example.

Keywords: Chemisorption, Copper, Density functional calculations, Ab-initio quantum chemical methods and calculations, Hydrogen, Low index single crystal surfaces, Models of surface chemical reactions

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I. INTRODUCTION AND COMPUTATIONAL METHOD

In recent years, the application of first principles electronic structure methods to surface systems has increased significantly as a result of improvements in algorithms and enhanced computational speed. The system size and complexity which can be analysed has increased by an order of magnitude following the pioneering work of Car and Parrinello [1], who introduced an iterative minimisation of the total energy based on wavefunction improvements at each iteration. The construction of the initial wavefunction is clearly important for efficiency in such an approach.

Among several different approaches, there are two simple and natural choices of basis set for the expansion of electron wavefunctions: atomic orbitals and plane waves. On the negative side, atomic orbital methods have difficulties in representing the wavefunctions and potential in interstitial and vacuum regions while plane wave expansions are expensive for representing localised atomic character, for example 3d wavefunctions. Nevertheless, plane-wave basis sets are in most common use since they are simple, independent of atomic positions, fast Fourier transformation (FFT) methods can be applied readily, and accuracy can be systematically improved by including additional plane waves with higher energy cut-offs. Although atomic orbitals are more physical it is difficult to represent uniform charge density, as in the vacuum region of a surface, with atom-centered, localised orbitals. On the other hand, plane-wave basis sets are also inefficient in a surface calculation using a slab geometry, since one needs as many plane waves for the vacuum as for the solid region. Therefore, a combination of the important properties of plane waves with atomic orbitals in a mixed basis may give a convenient and efficient representation, especially for systems which include both highly localised (atomic-like) and delocalised (plane-wave-like) components.

In this study, we have implemented a mixed-basis approach [2] which uses pseudo-atomic orbitals and a few low-energy plane waves as the basis set within a density functional, pseudopotential calculation. A similar approach has been described by Neugebauer and Van de Walle [3], but they focussed on providing a better starting wavefunction for a full
The Kohn-Sham eigenfunctions are expanded as

$$\psi_{\alpha \vec{k}}(\vec{r}) = \sum_{\mu} a_{\mu}^\alpha(\vec{k}) \chi_\mu(\vec{r}) + \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} b_{\vec{G}}^\alpha e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}$$

(1)

where $\alpha$ is the band index, $\mu$ is a combined index which labels the orbitals and atomic sites, $a$ and $b$ are coefficients of the pseudo-atomic orbitals and plane waves, respectively, and $\Omega$ is the volume of the unit cell. $\chi_\mu$ is the Bloch sum formed from pseudo-atomic orbitals as

$$\chi_\mu(\vec{r}) \equiv \chi_{\mu m}^i(\vec{r}) = \sum_{\vec{R}_l} e^{i\vec{k} \cdot (\vec{R}_l + \vec{\tau}_i)} \phi_m(\vec{r} - \vec{R}_l - \vec{\tau}_i)$$

(2)

where $m$ labels the orbitals, the $\vec{R}_l$ are the lattice vectors, the $\vec{\tau}_i$ are the atomic coordinates, and $\phi_m$ are pseudo-atomic orbitals. In practice, we use a plane-wave expansion for $\chi_\mu(\vec{r})$, and exactly the same FFT grid as in a full plane-wave calculation. There are therefore two plane-wave energy cut-offs to be considered in the mixed-basis calculation. The larger one is the cut-off used in the representation of $\chi_\mu(\vec{r})$ and is the same as would be used in a full plane-wave calculation. The smaller one is the cut-off for the extra, low-energy plane waves which appear in the second term of Eq. (1). This plane-wave representation of $\chi_\mu(\vec{r})$ makes the calculation of the charge density, the kinetic energy, multicentre integrals, and the contribution from non-local pseudopotentials straightforward.

Solving the Schrödinger equation then reduces to solving the secular equation

$$\text{det}|H - SE| = 0.$$  

(3)

The overlap matrix elements are given by (with reference to the partition of $\psi$ in Eq. (1))

$$S_{\vec{G}\vec{G}'} = \delta_{\vec{G},\vec{G}'}$$  

(4)

$$S_{\mu\vec{G}} = e^{-i\vec{G} \cdot \vec{\tau}_i} I_{m}^{\mu}(\vec{k})$$  

(5)

$$S_{\mu\nu} = \sum_{\vec{g}} e^{-i\vec{G} \cdot (\vec{\tau}_i - \vec{\tau}_j)} I_{\vec{g}}^{\mu\nu}(\vec{k}) I_{\vec{g}}^{\mu\nu}(\vec{k})$$  

(6)
where $\nu \equiv (n, j)$ and $I^m_{\vec{g}}(\vec{k})$ is the Fourier integral of the pseudo-atomic orbital,

$$I^m_{\vec{g}}(\vec{k}) = \frac{1}{\sqrt{\Omega}} \int d\vec{r} e^{-i(\vec{k} + \vec{g}).\vec{r}} \phi_m(\vec{r}).$$  \hspace{1cm} (7)

Similarly, the Hamiltonian matrix elements are based on a plane-wave representation

$$H_{\vec{G}\vec{G}'} = \frac{1}{\sqrt{\Omega}} \int d\vec{r} e^{-i(\vec{k} + \vec{G}).\vec{r}} \hat{H} e^{i(\vec{k} + \vec{G}).\vec{r}}$$
\hspace{1cm} (8) 

$$= |\vec{k} + \vec{G}|^2 \delta_{\vec{G}, \vec{G}'} + V_{\text{local}}(\vec{G} - \vec{G}') + V_{NL}((\vec{k} + \vec{G}), (\vec{k} + \vec{G}')).$$  \hspace{1cm} (9)

Then

$$H_{\mu\vec{G}} = \sum_{\vec{g}} e^{-i\vec{g}.\vec{r}_i} I^m_{\vec{g}}(\vec{k}) H_{\vec{g}\vec{G}}$$  \hspace{1cm} (10) 

$$H_{\mu\nu} = \sum_{\vec{g}\vec{g}'} e^{i\vec{g}'\cdot\vec{r}_j} e^{-i\vec{g}\cdot\vec{r}_i} I^n_{\vec{g}'}(\vec{k}) I^m_{\vec{g}}(\vec{k}) H_{\vec{g}'\vec{G}}$$  \hspace{1cm} (11)

The local part of the potential, $V_{\text{local}}$, in Eq. 9 contains the Hartree and exchange-correlation potentials, as well as the local part of the pseudopotential. In practice, only the Hartree and exchange-correlation contributions need be re-calculated through the self-consistency cycle—the pseudopotential (both local and non-local, $V_{NL}$ parts) and kinetic energy matrix elements are calculated only at the first iteration. Self-consistency is achieved by a combination of Kerker charge density mixing and a modified Broyden method \cite{4,5}. The initial charge density is constructed from overlapping, atomic pseudo-charge densities.

Diagonalization of Eq. 3 is acceptable, since there are at most 9 orbitals (s,p,d) for each atom, and typically 10 to 20 additional plane waves per atom (see below). This results in a matrix size less than $10^3 \times 10^3$, even for a moderately large system, compared to between $10^4$ to $10^5$ for a pure plane-wave expansion. In fact, for the H$_2$/Cu system considered below, the most expensive part of the whole calculation is the construction of the Hamiltonian matrix. Tests on this system show that the mixed-basis method is 6 to 8 times faster per iteration than our pure plane wave code (as described in \cite{6}). In addition, it typically requires fewer than half as many iterations to converge, and so provides a significant improvement in computational speed. A full analysis of the timing and scaling of the computation with respect to the important calculational parameters will be presented elsewhere.
II. CALCULATIONS AND RESULTS

We have carried out a careful benchmarking analysis of the mixed-basis approach by increasing the number of additional low-energy plane-waves and comparing the results with an exactly equivalent calculation based on plane waves only. The system chosen for this comparison is hydrogen dissociation on Cu(111), which is a model system for the experimental (e.g. [7]) and theoretical (e.g. [8–10]) study of dissociation dynamics. In particular, we concentrate on the value of the minimum energy barrier, which is known to occur for the geometry in which the molecular axis is parallel to the surface plane and with the H$_2$ molecule over a bridge site with the H atoms pointing towards neighbouring hollow sites [8]. In all calculations the transition state is taken to be where the H$_2$ molecule is 1.2Å above the top-layer Cu atoms, with a bond length of 1.1Å [10].

As a preliminary study, we have examined some properties of bulk fcc Cu and the H$_2$ molecule within the mixed-basis scheme. A semi-relativistic, Troullier-Martins [11] pseudopotential (with associated pseudo-atomic orbitals) is used to describe the Cu atoms, and hydrogen is described by the full Coulombic potential, with localised 1s and 2p orbitals. For Cu, the irreducible wedge of the fcc Brillouin zone is sampled with 28 $\vec{k}$-points and the H$_2$ molecule is calculated in the same cell as in the H$_2$/Cu(111) system described below. The calculated lattice parameter and bulk modulus for Cu; and bond length and vibrational frequency (estimated from a harmonic fit about the equilibrium bond length) for H$_2$ are presented in Tables I and II respectively, as a function of the cut-off energy for the low-energy plane waves. It can be seen that for these two very different systems the mixed-basis method converges rapidly to the full plane-wave result.

Technical details of the full H$_2$/Cu(111) calculation are as follows. The substrate is modelled by a 5 layer, rigid Cu slab with the experimental lattice parameter of 3.61Å. There are 3 Cu atoms per layer within a $\sqrt{3} \times \sqrt{3}$ geometry and 4 layers of vacuum separate the slabs. An H$_2$ molecule is placed on only one side of the slab. The surface Brillouin zone is sampled by 54 special $\vec{k}$-points (15 in the irreducible wedge), and the Fermi surface
is broadened with a 0.25eV smearing function, with the total energy being extrapolated to zero temperature. A cut-off of 800eV is used for the pure plane-wave calculation, and for the representing the localised orbitals in the mixed-basis method. These calculational parameters should provide well-converged results for the energy barrier [10]. The local density approximation (LDA) is used in the self-consistency cycle of the calculations, and the generalised gradient approximation (GGA) (see eg [12]) is incorporated by calculating the exchange-correlation energy of the LDA density.

Six values of the minimum barrier have been calculated. Five use the mixed-basis approach with different numbers of additional plane waves, corresponding to energy cut-offs of 0eV (ie pure pseudo-atomic orbitals), 20eV, 40eV, 60eV and 80eV. The typical number of additional plane waves are 0, 65, 180, 330 and 520 respectively for these cut-offs. The sixth value corresponds to the full plane-wave calculation. Computed values of the minimum energy barrier are given in Table III. It can be seen that the mixed-basis method provides an accurate value for the barrier height (within 10 meV) once plane waves with energies up to 40 eV are included.

III. CONCLUSIONS

The mixed-basis method we have presented appears to provide an accurate and computationally cheap alternative to full plane-wave methods for first principles calculations of surface systems. Although we have discussed only a single case in detail, tests on a variety of systems have confirmed the generality of this approach, with structural parameters being accurate to of order 0.01Å and energy differences accurate to a few tens of meV. Only total energies have been discussed here, but it is also straightforward to calculate forces within the mixed-basis scheme using the general force expressions given in [13]. This holds out the prospect of being able to perform, with high computational efficiency, a full structural relaxation of a system using the mixed-basis approach. If required, the calculation can then be “finished off” using a full plane-wave expansion, in which case the mixed-basis method
will provide an accurate starting structure and highly optimised initial wavefunctions.

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TABLES

| Energy cut-off (eV) | Lattice constant (Å) | Bulk Modulus (GPa) |
|--------------------|----------------------|-------------------|
| AO                 | 3.59                 | 165               |
| 20                 | 3.57                 | 180               |
| 40                 | 3.57                 | 177               |
| 60                 | 3.58                 | 173               |
| 80                 | 3.58                 | 175               |
| PW                 | 3.57                 | 178               |

TABLE I. Calculated LDA lattice constant and bulk modulus for fcc Cu, as a function of the cut-off energy for additional plane waves in the mixed-basis approach. AO represents the pure pseudo-atomic orbital limit (ie 0 eV cut-off) and PW the full plane-wave limit (with plane waves up to 800 eV). The Murnaghan equation of state is used.

| Energy cut-off (eV) | Bond length (Å) | Vibrational quantum (meV) |
|--------------------|-----------------|---------------------------|
| AO                 | 0.837           | 535                       |
| 20                 | 0.781           | 489                       |
| 40                 | 0.761           | 471                       |
| 60                 | 0.756           | 467                       |
| 80                 | 0.754           | 464                       |
| PW                 | 0.753           | 462                       |

TABLE II. Calculated GGA bond length and vibrational quantum ($\hbar\omega$) for $\text{H}_2$. Symbols are as in Table I.
| Energy cut-off (eV) | Barrier Height (eV) |
|--------------------|--------------------|
| AO                 | -0.854             |
| 20                 | 0.520              |
| 40                 | 0.606              |
| 60                 | 0.614              |
| 80                 | 0.620              |
| PW                 | 0.612              |

TABLE III. GGA minimum energy barrier for H$_2$ dissociation on Cu(111). Symbols are as in Table I.