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***Ab initio* molecular dynamics in adaptive coordinates**

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We present a formulation of *ab initio* molecular dynamics that exploits the efficiency of plane waves in adaptive curvilinear coordinates, and thus provides an accurate treatment of first-row elements. The method is used to perform a molecular-dynamics simulation of the CO<sub>2</sub> molecule, and allows the reproduction of detailed features of its vibrational spectrum such as the splitting of the Raman  $\sigma_g^+$  mode caused by Fermi resonance. This approach opens the way to highly accurate *ab initio* simulations of organic compounds.

An increasing number of applications of *ab initio* molecular dynamics (MD) has given considerable insight into dynamical and statistical properties of a wide range of materials.<sup>1</sup> However, the application of this method to important fields such as organic chemistry, or to the study of oxide materials, has been hindered by difficulties in representing accurately first-row elements using plane waves and pseudopotentials. Implementations of *ab initio* MD based on plane waves are intrinsically limited by the slow convergence of the Fourier expansions of wave functions and potentials. This limitation is particularly severe in the case of first-row elements for which both wave functions and potentials are rapidly varying. Although some progress has been made recently to circumvent this problem by introducing modified pseudopotentials for first-row elements,<sup>2,3</sup> a unified approach treating all atomic species on the same footing, and ensuring the same accuracy and transferability of all potentials in various environments is still lacking. A method which relies on well-established norm-conserving pseudopotentials,<sup>4</sup> and does not necessitate special approximations for the representation of first-row elements is essential, e.g., for the study of materials under high pressure, or for MD simulations carried out at high temperatures. In such situations, interatomic distances can become substantially smaller than equilibrium distances, which requires a high transferability of pseudopotentials. Furthermore, it would be highly desirable to take advantage of the large body of information accumulated over the years about conventional norm-conserving pseudopotentials.

In this paper, we present a formulation of *ab initio* MD, which exploits the efficiency of plane waves in adaptive curvilinear coordinates, and therefore allows for an accurate treatment of all elements using conventional norm-conserving pseudopotentials. An application to the calculation of vibrational properties of the CO<sub>2</sub> molecule yields results comparable to those obtained with the most elaborate quantum chemistry methods, but also allows us to observe

anharmonic effects on its vibrational spectrum.

Our approach is based on the method of plane waves in adaptive coordinates which was recently proposed<sup>5,6</sup> to perform highly accurate electronic structure calculations, within the density functional, pseudopotential formalism. This method has been successfully applied to the determination of the equilibrium configuration of small molecules containing first-row elements<sup>6</sup> and to selected phases of SiO<sub>2</sub>.<sup>7</sup> The basis set used in this method consists of plane waves in curvilinear coordinates,

$$\chi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{\Omega}} \left| \frac{\partial \xi}{\partial \mathbf{x}} \right|^{\frac{1}{2}} \exp[i\mathbf{k} \cdot \xi(\mathbf{x})], \quad (1)$$

where  $|\partial \xi / \partial \mathbf{x}|$  is the determinant of the Jacobian of the coordinate transformation  $\mathbf{x} \rightarrow \xi(\mathbf{x})$ , and  $\mathbf{k}$  is a reciprocal lattice vector. The functions  $\chi_{\mathbf{k}}(\mathbf{x})$  reduce to ordinary plane waves in the limit where  $\mathbf{x}(\xi) = \xi$ , i.e., when the coordinates are Euclidean. They form a complete and orthonormal basis for any choice of coordinates. In the approach of Ref. 6, coordinates are allowed to adapt freely so as to minimize the total energy. This implies that the basis set does not depend explicitly on ionic positions, so that no Pulay forces on ions have to be calculated. It also allows for an optimal adaptation of the basis set, and therefore leads to a rapid convergence of the calculation as the number of basis functions is increased. In its original formulation, the method of adaptive coordinates could be applied to *ab initio* MD simulations by either (i) reoptimizing the coordinates and the electronic wavefunction coefficients at every ionic step, or (ii) assigning a fictitious mass to the coordinates and solving a second order equation of motion for the electronic, ionic, and coordinate degrees of freedom. The first approach is workable,<sup>8</sup> although in practice a very accurate minimization of electronic and coordinate degrees of freedom must be performed at each ionic step in order to avoid the accumulation of systematic errors. The second approach, although it can be used

successfully in a simulated annealing search for minimum energy configurations, is not applicable for MD simulations since a large fictitious mass must be assigned to the coordinates in order to keep their dynamical evolution stable. When combined with usual integration time steps (5–10 a.u.) this large fictitious mass causes a sizable energy transfer to occur between the ionic and coordinate degrees of freedom during the MD simulation. As a consequence, the potential energy surface followed by the ions does not correspond to the Born-Oppenheimer surface, and the resulting ionic trajectories are meaningless. This energy transfer between degrees of freedom could be avoided by using very small time steps, although this leads in practice to an unacceptably large number of steps.

Another approach consists in noting that efficient basis sets can also be defined by choosing *explicitly* the coordinate transformation  $\xi \rightarrow \mathbf{x}(\xi)$ . In what follows, we define  $\mathbf{x}(\xi)$  in such a way that the effective plane wave energy cutoff is increased in a prescribed way near atomic positions. The coordinate transformation  $\mathbf{x} \rightarrow \xi(\mathbf{x})$  is defined by specifying its *inverse*, i.e.,

$$\xi^i = x^i - \sum_{\alpha} f_{\alpha}^i(\mathbf{x} - \mathbf{R}_{\alpha}), \quad (2)$$

where  $\mathbf{R}_{\alpha}$  is the position of atom  $\alpha$ , and  $f_{\alpha}^i$  describes the deformation of coordinates around atom  $\alpha$  in the direction  $i$ . The form chosen for the functions  $f_{\alpha}^i$  must be such as to increase the effective energy cutoff on the atomic site  $\mathbf{R}_{\alpha}$ . We use the following definition:

$$f_{\alpha}^i(\mathbf{x} - \mathbf{R}_{\alpha}) = -(x^i - R_{\alpha}^i) f_{\alpha}(|\mathbf{x} - \mathbf{R}_{\alpha}|), \quad (3)$$

where  $f_{\alpha}(r)$  is a positive, rapidly decaying function. The definition of  $\xi(\mathbf{x})$  is then given by

$$\xi^i = x^i + \sum_{\alpha} (x^i - R_{\alpha}^i) f_{\alpha}(|\mathbf{x} - \mathbf{R}_{\alpha}|). \quad (4)$$

The Jacobian of the coordinate transformation, which is directly related to the plane wave effective energy cutoff,<sup>6</sup> can be computed directly from the  $f_{\alpha}^i$ 's,

$$\frac{\partial \xi^i}{\partial x^j} = \delta_{ij} + \sum_{\alpha} \left[ \delta_{ij} f_{\alpha}(|\mathbf{x} - \mathbf{R}_{\alpha}|) + \frac{(x^i - R_{\alpha}^i)(x^j - R_{\alpha}^j)}{|\mathbf{x} - \mathbf{R}_{\alpha}|} \frac{\partial f_{\alpha}(r)}{\partial r} \Big|_{r=|\mathbf{x} - \mathbf{R}_{\alpha}|} \right]. \quad (5)$$

The Jacobian (5) is symmetric, which implies in particular that the coordinates are curl-free

$$\frac{\partial \xi^i}{\partial x^j} - \frac{\partial \xi^j}{\partial x^i} = 0.$$

Various choices can be made for the definition of the function  $f_{\alpha}(r)$ . We use

$$f_{\alpha}(r) = A_{\alpha} \operatorname{sech} \frac{r}{a_{\alpha}}, \quad (6)$$

where  $a_{\alpha}$  is a parameter defining the range over which the energy cutoff is increased around atom  $\alpha$ .<sup>9</sup> The constant  $A_{\alpha}$  is chosen so as to reproduce a given maximum energy cutoff  $E_{\text{cut}}^{\alpha}$  at the atomic site and is given by

$$A_{\alpha} = \left( \frac{E_{\text{cut}}^{\alpha}}{E_{\text{cut}}^0} \right)^{\frac{1}{2}} - 1, \quad (7)$$

where  $E_{\text{cut}}^0$  is the plane wave energy cutoff in Euclidean coordinates. The choice of the value of  $a_{\alpha}$  is not critical. It can be deduced, e.g., from a calculation of the electronic structure of an isolated atom carried out with fully adaptive coordinates. The coordinates  $\mathbf{x}(\xi)$ , which are needed for the calculation of the total electronic energy, are then obtained by solving the nonlinear equation (4) iteratively using Newton's method, and by taking advantage of the fact that the Jacobian matrix (5) is known analytically. The solution of Eq. (4) must be repeated whenever atomic positions are updated during a MD simulation. Clearly, the solution obtained for the previous atomic positions provides a good starting point for the iterative solution of Eq. (4), and in practice, only a few iterations are necessary. The basis set defined by these coordinates depends only on ionic positions and on the functions  $f_{\alpha}$ . This effectively constrains the regions of enhanced energy cutoff to follow smoothly the atoms during the course of a MD simulation, ensuring a proper description of the electronic wave functions in the vicinity of atoms. Using such an explicit choice of coordinates will in general lead to a basis set which is less optimal than in the fully adaptive approach. However, since the basis set is complete for any choice of coordinates, the accuracy of the results can be improved systematically by increasing the value of  $E_{\text{cut}}^0$ .

Once the coordinates  $\mathbf{x}(\xi)$  are defined, all quantities needed for the calculation of the energy and of the forces on the electronic degrees of freedom can be deduced from them, and the procedure is identical to that presented in Ref. 6. Similarly, ionic forces can be calculated following Ref. 6, except for an additional Pulay term which comes from the explicit dependence of the basis set on atomic positions. The Pulay component of the force on the atomic coordinate  $R_{\alpha}^s$  is given by

$$F_{\alpha}^s = - \int \frac{\partial \xi^q}{\partial R_{\alpha}^s} \frac{\delta E}{\delta \xi^q} d^3 \xi,$$

where

$$\frac{\delta E}{\delta \xi^q} = \frac{\partial x^p}{\partial \xi^q} \frac{\delta E}{\delta x^p}$$

and summation over repeated indices is implied. The quantities  $\delta E / \delta x^p$  are the forces acting on coordinates, which are described in detail in Ref. 6.

This approach was used to calculate the vibrational spectrum of the CO<sub>2</sub> molecule, a prototypical example of small organic molecule. In spite of its small size, the calculation of its vibrational properties including anharmonic effects already represents a difficult test case for traditional *ab initio* quantum chemistry methods.<sup>10</sup> We used norm-conserving, nonlocal pseudopotentials,<sup>11</sup> in their separable form,<sup>12</sup> and the local density approximation (LDA) for exchange and

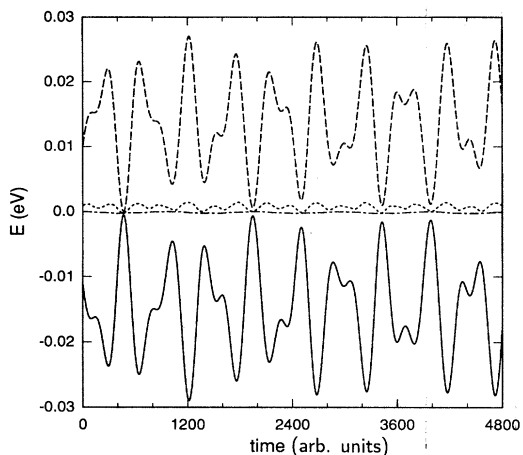


FIG. 1. Evolution of the Kohn-Sham energy (solid line), the ionic kinetic energy (dashed line), and the fictitious electronic kinetic energy (dotted line) during part of the MD simulation. The total energy (dash-dotted line) shows fluctuations of the order of  $10^{-4}$  eV and no noticeable drift.

correlation.<sup>13,14</sup> The parameters defining the coordinates were  $a_\alpha = 1.4$  a.u. and  $A_\alpha$  was chosen so as to produce an effective plane wave energy cutoff of 90 Ry on oxygen and 40 Ry on carbon, starting from an initial Euclidean energy cutoff of  $E_{\text{cut}}^0 = 20$  Ry. The molecule was placed in a simulation cell of  $18 \times 14 \times 14$  a.u. and the ground state electronic structure of  $\text{CO}_2$  was first determined in a fixed asymmetric ionic configuration corresponding to a small distortion away from its equilibrium geometry, and involving all three modes of deformation of the molecule (bending, symmetric, and antisymmetric stretching). The MD simulation was started with an equilibration run of 0.1 ps, followed by a MD simulation of 0.2 ps during which ionic trajectories were collected. The behavior of the Kohn-Sham energy, the kinetic energy of ions, the fictitious kinetic energy of the electrons, and the total energy are shown in Fig. 1 for a fraction of the

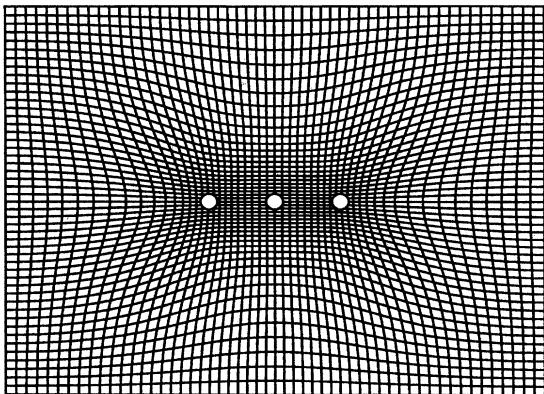


FIG. 2. Image of a regularly spaced rectangular grid in  $\xi$  space under the map  $\mathbf{x}(\xi)$ , calculated in a plane containing the  $\text{CO}_2$  molecule. The left and right circles represent oxygen atoms, and the center circle represents the carbon atom.

TABLE I. Vibrational frequencies of  $\text{CO}_2$  as obtained from *ab initio* simulations carried out with  $E_{\text{cut}}^0 = 20$  Ry and 30 Ry, and from experiment (Expt.).

|                            | $\pi_u$ | $\sigma_g^+$ | $\sigma_u^+$ |
|----------------------------|---------|--------------|--------------|
| $E_{\text{cut}}^0 = 20$ Ry | 624     | 1356,1386    | 2310         |
| $E_{\text{cut}}^0 = 30$ Ry | 642     | 1368,1428    | 2353         |
| Expt.                      | 667     | 1286,1388    | 2349         |

total simulation time. The absence of any noticeable drift in the total energy confirms that the equations of motion for both ions and electrons are integrated accurately. In order to illustrate a typical coordinate transformation  $\mathbf{x}(\xi)$ , we show in Fig. 2 a snapshot of  $\mathbf{x}(\xi)$  in a plane containing the molecule.

The vibrational spectrum of  $\text{CO}_2$  was calculated from the data collected during the 0.2 ps simulation using the maximum entropy method<sup>17</sup> with 150 poles in the fitting procedure, and then used to extract vibrational frequencies. The experimentally measured low-frequency vibrational spectrum of  $\text{CO}_2$  consists of two infrared active modes at  $667 \text{ cm}^{-1}$  ( $\pi_u$ ) and  $2349 \text{ cm}^{-1}$  ( $\sigma_u^+$ ), and a Raman  $\sigma_g^+$  doublet at  $1286$  and  $1388 \text{ cm}^{-1}$  split by Fermi resonance.<sup>15</sup> This splitting is caused by a strong enhancement of anharmonic coupling between the  $\sigma_g^+$  and  $\pi_u$  modes which originates in the near degeneracy of the overtone of the  $\pi_u$  mode with the fundamental of the  $\sigma_g^+$  mode. Reproducing this splitting clearly represents a challenge for any *ab initio* method.

After the first 0.05 ps of MD simulation, the calculated power spectrum already exhibits peaks near  $630$  and  $2380 \text{ cm}^{-1}$ , which can be assigned to the  $\pi_u$  and  $\sigma_u^+$  modes, respectively. Another peak corresponding to the  $\sigma_g^+$  mode appears near  $1400 \text{ cm}^{-1}$  and is broader, indicating mixing between the fundamental of the  $\sigma_g^+$  mode and the overtone of the  $\pi_u$  mode. After completion of the MD simulation, we observe sharp  $\pi_u$  and  $\sigma_u^+$  peaks at  $624$  and  $2310 \text{ cm}^{-1}$ , respectively, whereas the  $\sigma_g^+$  Raman peak splits into two well resolved peaks at  $1356$  and  $1392 \text{ cm}^{-1}$ . The magnitude of the splitting between the two Raman peaks is comparable to the experimental splitting. However, since the present simulation treats the ions classically, a more detailed com-

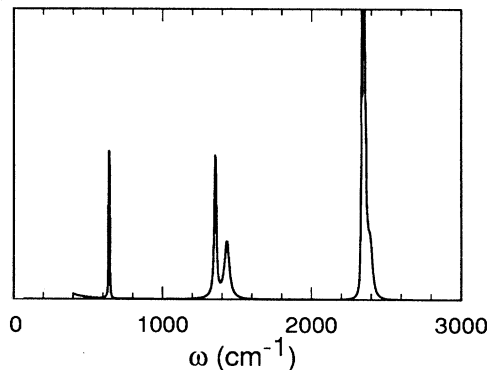


FIG. 3. Power spectrum of the vibrations of the  $\text{CO}_2$  molecule extracted from a trajectory of 0.2 ps. The splitting of the symmetric stretching mode around  $1400 \text{ cm}^{-1}$  is clearly visible.

parison with experiment would be meaningless. The calculated center of gravity of the Raman doublet lies at  $1371\text{ cm}^{-1}$ , to be compared to an experimental value of  $1337\text{ cm}^{-1}$ . In order to check the convergence of the above results, the full simulation was repeated starting from an initial energy cutoff ( $E_{\text{cut}}^0$ ) of 30 Ry, which produces a maximum energy cutoff ( $E_{\text{cut}}^{\alpha}$ ) of 138 Ry on oxygen atoms. The resulting frequencies are 642, 1368, 1428, and  $2353\text{ cm}^{-1}$  for the  $\pi_u$ , the Raman  $\sigma_g^+$  doublet, and the  $\sigma_u^+$  modes, respectively. The agreement with experiment improves for the  $\pi_u$  and  $\sigma_u^+$  modes, but degrades slightly for the Raman doublet. Errors in the calculated frequencies are of the order of  $40\text{ cm}^{-1}$  for the  $\pi_u$  and for the higher mode of the Raman doublet, and  $80\text{ cm}^{-1}$  for the lower mode of the Raman doublet—the smaller error ( $4\text{ cm}^{-1}$ ) obtained for the  $\sigma_u^+$  mode being considered fortuitous. These results are summarized in Table I and the power spectrum is shown in Fig. 3. This kind of agreement with experiment is excellent for a first principles approach.

Quantum chemistry methods based on energy gradients have been used to compute the *harmonic* vibrational frequencies of  $\text{CO}_2$  including various combinations of basis sets and treatments of electronic correlations.<sup>18</sup> Harmonic frequencies cannot be compared directly to experiment, but only to frequencies deduced by fitting a potential energy function to experimental results.<sup>16</sup> Although frequencies obtained at the SCF level are unsatisfactory—errors can be as

large as  $150\text{ cm}^{-1}$ —the errors obtained with the coupled-cluster methods<sup>19</sup> are smaller than  $30\text{ cm}^{-1}$ , an accuracy comparable to that of our results. We conclude that, in the case of  $\text{CO}_2$ , the LDA treatment of exchange and correlation yields excellent results, which are comparable to those of the most accurate methods of quantum chemistry. Furthermore, the ability to perform *ab initio* MD allows one to observe anharmonic behavior such as the Fermi resonance discussed above. MD simulations are beyond the present capabilities of quantum chemistry methods.

In conclusion, we have presented a formulation of *ab initio* molecular dynamics which uses plane waves in adaptive coordinates. This approach allows us to treat all atoms in the simulation on an equal footing, using norm-conserving, non-local pseudopotentials. The large enhancement of the plane wave effective energy cutoff achieved near atoms allows one to use conventional pseudopotentials without any compromise on their transferability. A calculation of the vibrational spectrum of  $\text{CO}_2$  demonstrates the accuracy of the method and its applicability to *ab initio* MD simulations of organic compounds. A study of the equilibrium and vibrational properties of a simple carbohydrate molecule using this approach is under way.<sup>20</sup>

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<sup>1</sup>R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985). For reviews, see, e.g., G. Galli and M. Parrinello, in *Computer Simulation in Materials Science*, edited by M. Meyer and V. Pontikis (Kluwer, Dordrecht, 1991), pp. 283–304, and M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

<sup>2</sup>N. Trouiller and J.-L. Martins, Phys. Rev. B **43**, 1993 (1991).

<sup>3</sup>D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

<sup>4</sup>D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

<sup>5</sup>F. Gygi, Europhys. Lett. **19**, 617 (1992).

<sup>6</sup>F. Gygi, Phys. Rev. B **48**, 11 692 (1993).

<sup>7</sup>D. R. Hamann, Phys. Rev. B **51**, 7337 (1995).

<sup>8</sup>F. Gygi (unpublished).

<sup>9</sup>Other functions have been tried and yield equally good results, e.g.,  $f_{\alpha}(r) = A_{\alpha}(a_{\alpha}/r)\tanh(r/a_{\alpha})\exp[-(r/b_{\alpha})^2]$ , where  $a_{\alpha}$  is the range of enhancement of the energy cutoff and  $b_{\alpha}$  determines a distance over which Euclidean coordinates are recovered.

<sup>10</sup>For a discussion of *ab initio* quantum chemistry calculations of vibrational properties, see, e.g., C. E. Dykstra, *Ab initio Calculation of the Structures and Properties of Molecules, Studies in*

*Physical and Theoretical Chemistry* (Elsevier, Amsterdam 1988), Vol. 58.

<sup>11</sup>The pseudopotential of oxygen is taken from Ref. 4. For carbon, we use the potential of Giannozzi, whose parameters are given in W. Andreoni, D. Scharf, and P. Giannozzi, Chem. Phys. Lett. **173**, 449 (1990).

<sup>12</sup>L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

<sup>13</sup>D. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).

<sup>14</sup>J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

<sup>15</sup>G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, London, 1968), Vol. II.

<sup>16</sup>Z. Cihla and A. Chedin, J. Mol. Spectrosc. **40**, 337 (1971).

<sup>17</sup>W. H. Press, B. P. Flannery, S. A. Teukosky and W. T. Vetterling, *Numerical Recipes, The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1986).

<sup>18</sup>J. R. Thomas *et al.*, J. Chem. Phys. **99**, 403 (1993).

<sup>19</sup>For a description of coupled cluster methods, see, e.g., R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).

<sup>20</sup>F. Gygi (unpublished).

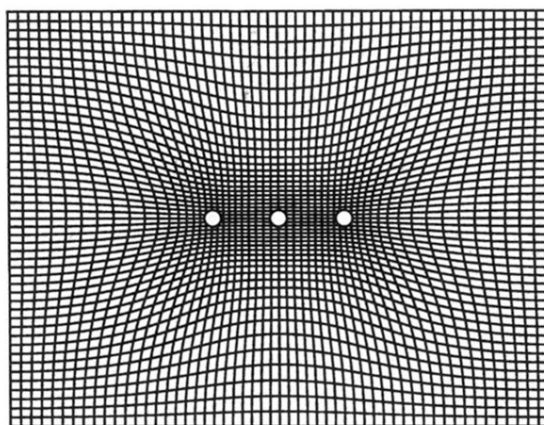


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