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# Vibrations of adsorbates on metal surfaces from geometry optimizations

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We present a method to compute harmonic vibrations that uses the structures and the forces in the structures that are obtained from a geometry optimization. It does not require any additional electronic structure calculations. The method generally takes only on the order of minutes on a regular PC, but it does not guarantee the calculation of all vibrations of a system. Tests on small adsorbates on a transition metal surface show, however, that the most relevant vibrations are obtained. An important part of the method is the inclusion of several checks to determine the reliability of its results, which gives also error estimates of the vibrational frequencies.

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## I. INTRODUCTION

Most electronic structure calculations of molecules adsorbed on metal surfaces as encountered in heterogeneous catalysis and surface science are nowadays done using density-functional theory with a periodic slab and a plane-wave basis set [1]. Such calculations readily yield energies and forces but not frequencies. The usual approach is to use a finite-difference scheme [2]. After the geometry is optimized and a structure corresponding to a minimum of the potential-energy surface is determined, the atoms are systematically displaced along the coordinate axes. The force-constant matrix  $\mathbf{F}$  can then be determined using

$$\mathbf{F}_{mm} = \frac{f_n(\mathbf{r}^{(0)} - \Delta\mathbf{e}_m) - f_n(\mathbf{r}^{(0)} + \Delta\mathbf{e}_m)}{2\Delta}, \quad (1)$$

where  $f_n$  is the force along coordinate  $n$ ,  $\mathbf{r}^{(0)}$  are all coordinates of the minimum, and  $\Delta\mathbf{e}_m$  is a displacement over  $\Delta$  along coordinate  $m$ . This expression gives correct results if the minimum  $\mathbf{r}^{(0)}$  is determined accurately and if there are no anharmonicities. The latter means making sure  $\Delta$  is not too large. However, if  $\Delta$  is too small, then the denominator may blow up the numerical noise in the forces and lead to large errors in the force-constant matrix. Reasonable values for  $\Delta$  are known nowadays. Because  $\mathbf{F}_{nm} = \mathbf{F}_{mn}$  must hold, a comparison between these quantities calculated with the expression above gives information on how accurate one can expect the results to be. Note that we say nothing here about errors that are due to the approximations in the method that is used to do the electronic structure calculation. We are here only concerned about how to determine vibrations from the calculated energies and forces and the errors that are made in the procedure that is used for that; i.e., we pretend that the results from the electronic structure calculations are exact, apart from some possible numerical noise.

The drawback of the finite-difference scheme that we want to address here is the computational costs. If there are  $N_{\text{coord}}$  coordinates in a system and if we assume that a single-point calculation yields all components of the forces, then we need to do two single-point calculations per column of the force-constant matrix, one with a displacement  $\Delta\mathbf{e}_m$  and one with  $-\Delta\mathbf{e}_m$ . This means we need to do  $2N_{\text{coord}}$  single-point calculations. We claim that in many cases these calculations

need not be done at all. When we are dealing with a molecule adsorbed on a metal surface, we are generally only interested in the vibrations of that molecule and most of the time even only in a few particular vibrations of that molecule. The coordinates that change in those vibrations are generally also those that change most in a geometry optimization. That means that we may be able to extract the potential-energy surface for the interesting vibrations from energies and forces that were generated during the geometry optimization. The method that we will describe in this paper does just that. It first analyzes the results generated by a geometry optimization and determines the subspace of the whole configuration space for which a useful potential-energy surface can be constructed. Then it computes the vibrations in that subspace. And finally it does an error analysis for these vibrations. We would like to stress that our method does not yield all vibrations. However, it takes very little time. It is an interactive computation on a PC that normally takes only a few minutes. One can always decide to do a full normal mode analysis, but we have found that in most of our cases a calculation of all vibrations as described above was no longer necessary.

This paper is structured as follows. Section II describes the method. It deals with how to determine the subspace of configuration space for which one can construct a potential-energy surface, how to determine the vibrations from that potential-energy surface, and how to assess the reliability of those vibrations. Section III illustrates the method by discussing two examples. One example is a regular minimum of a potential-energy surface, but the other example is a structure for which one wants to know if it is a transition state. Finally Sec. IV draws some conclusions and discusses the applicability of our method to other systems and how the method can be extended if one wants to compute all vibrations. The Appendixes deal with some mathematical details left out of Sec. II.

## II. THEORY

### A. Mathematical formulation of the problem

Suppose we have a set of  $N_{\text{struct}}$  structures  $\{\mathbf{r}_\alpha\}$  with  $\alpha = 1, 2, \dots, N_{\text{struct}}$  and each  $\mathbf{r}_\alpha$  a vector containing all

Cartesian coordinates of the system. One way to obtain such a set is by doing a geometry optimization, but we will not restrict ourselves to this situation. We will assume that, apart from the coordinates, we also have the forces  $\{\mathbf{f}_\alpha\}$  for all structures. To compute vibrations we need a potential-energy surface (PES). For the harmonic vibrations this PES should be a harmonic force field of the form

$$V(\mathbf{r}) = V_0 + \mathbf{g}^T \mathbf{r} + \frac{1}{2} \mathbf{r}^T \mathbf{F} \mathbf{r}, \quad (2)$$

with  $V_0$  a constant,  $\mathbf{g}$  a vector with the gradient of the force field at  $\mathbf{r}=\mathbf{0}$ , and  $\mathbf{F}$  the force-constant matrix or Hessian. The forces for structure  $\mathbf{r}$  are given by [3]

$$\mathbf{f}(\mathbf{r}) = -\nabla V(\mathbf{r}) = -\mathbf{g} - \mathbf{F}\mathbf{r}, \quad (3)$$

where we have used the fact the  $\mathbf{F}$  is a symmetric matrix.

We would like the force field  $V$  to represent the forces  $\{\mathbf{f}_\alpha\}$  as accurately as possible. We therefore fit the force field  $V$  to the forces. We use a least-squares procedure and minimize

$$\chi^2 = \frac{1}{N_{\text{struct}} N_{\text{coord}}} \sum_{\alpha=1}^{N_{\text{struct}}} |\mathbf{f}(\mathbf{r}_\alpha) - \mathbf{f}_\alpha|^2 \quad (4)$$

as a function of the parameters in  $\mathbf{g}$  and  $\mathbf{F}$  of the harmonic PES. Here  $N_{\text{coord}}$  is the number of coordinates of the systems. The constant  $V_0$  cannot be obtained from the forces, because it does not affect  $\mathbf{f}(\mathbf{r}_\alpha)$ . On the other hand, the vibrations also do not depend on  $V_0$ .

If the structures  $\{\mathbf{r}_\alpha\}$  are arbitrary, it might not be possible to determine all parameters. The number of structures might be too small. The forces depend on  $N_{\text{coord}}$  parameters in  $\mathbf{g}$  and  $N_{\text{coord}}(N_{\text{coord}}+1)/2$  in  $\mathbf{F}$ . Differentiating  $\chi^2$  with respect to these parameters gives  $N_{\text{coord}}(N_{\text{coord}}+3)/2$  linear equations, which will not have a unique solution if the number of data for fitting is less than this number. The number of data equals the number of structures times the number of forces, or  $N_{\text{coord}} N_{\text{struct}}$ . So we have  $N_{\text{struct}} \geq (N_{\text{coord}}+3)/2$  as a necessary condition.

This condition is in general fulfilled if the structures are obtained from a geometry optimization, because minimizing the energy scales at best quadratically with the number of coordinates [4]. The condition will not necessarily be sufficient, however. A situation where it is not is when the optimal geometry is symmetric and the symmetry is known beforehand. The structures  $\{\mathbf{r}_\alpha\}$  from the geometry optimization will then also have the same symmetry. Consequently the forces will then contain no information on the PES that corresponds to structures of the system with a lower symmetry and vibrations that reduce the symmetry cannot be determined. This means that at best only vibrations that transform according to the total symmetric irreducible representation of the symmetry group can be determined [5]. More generally, we cannot determine vibrations in directions for which we have no information of the PES.

The problem is then to determine the linear subspace of configuration space for which  $\{\mathbf{r}_\alpha\}$  and  $\{\mathbf{f}_\alpha\}$  contain sufficient information to construct a harmonic PES. We split this problem into two parts. First, suppose that we know that the

dimension of this subspace equals  $N_{\text{dof}}$ . ( $N_{\text{dof}}$  stands for the number of degrees of freedom of the PES.) For the other  $N_{\text{coord}} - N_{\text{dof}}$  directions we assume that the PES is flat. We then need to determine  $\mathbf{g}$  and  $\mathbf{F}$ , which minimize  $\chi^2$  with the restriction that the rank of  $\mathbf{F}$  be at most  $N_{\text{dof}}$ . Second, by doing this for various values of  $N_{\text{dof}}$  and comparing the results we can determine the number of directions for which we can determine the PES reliably and determine the vibrations in these directions.

### B. Determining the force-constant matrix

We need to determine a PES with rank  $\mathbf{F} \leq N_{\text{dof}}$  for a given  $N_{\text{dof}}$ , and we need a way to compare the results for various values of  $N_{\text{dof}}$ . We start with the fit of the PES. For  $\mathbf{g}$  we can find a simple closed expression

$$\frac{\partial \chi^2}{\partial g_n} = -\frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} [f_n(\mathbf{r}_\alpha) - f_{\alpha,n}] = 0, \quad (5)$$

with  $g_n$  component  $n$  of the gradient,  $f_n(\mathbf{r}_\alpha)$  component  $n$  of the force according to Eq. (3) for structure  $\mathbf{r}_\alpha$ , and  $f_{\alpha,n}$  the same force but now from our electronic structure calculations. This leads to

$$\mathbf{g} = -\mathbf{F}\bar{\mathbf{r}} - \bar{\mathbf{f}}, \quad (6)$$

with

$$\bar{\mathbf{r}} = \frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} \mathbf{r}_\alpha \quad (7)$$

and

$$\bar{\mathbf{f}} = \frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} \mathbf{f}_\alpha. \quad (8)$$

Substitution of this expression into Eq. (4) gives

$$\chi^2 = \text{Tr}[\mathbf{F}^2 \mathbf{A}_{rr} + 2\mathbf{F}\mathbf{A}_{fr} + \mathbf{A}_{ff}], \quad (9)$$

with the following correlation matrices:

$$\mathbf{A}_{rr} = \frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} [\mathbf{r}_\alpha - \bar{\mathbf{r}}][\mathbf{r}_\alpha - \bar{\mathbf{r}}]^T, \quad (10)$$

$$\mathbf{A}_{fr} = \frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} [\mathbf{f}_\alpha - \bar{\mathbf{f}}][\mathbf{r}_\alpha - \bar{\mathbf{r}}]^T, \quad (11)$$

and

$$\mathbf{A}_{ff} = \frac{1}{N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} [\mathbf{f}_\alpha - \bar{\mathbf{f}}][\mathbf{f}_\alpha - \bar{\mathbf{f}}]^T. \quad (12)$$

Next we determine  $\mathbf{F}$ . (An alternative approach to the following can be found in Appendix A.) The trace in Eq. (9) does not change if we transform to another basis. In particular, if we take the basis that diagonalizes  $\mathbf{F}$ , we get

$$\chi^2 = \sum_{n=1}^{N_{\text{coord}}} [\varphi_n^2 a_n^{(rr)} + 2\varphi_n a_n^{(fr)} + a_n^{(ff)}], \quad (13)$$

where  $\varphi_n$  is an eigenvalue of  $\mathbf{F}$ ,  $a_n^{(rr)}$  is the  $n$ th matrix element on the diagonal of  $\mathbf{A}_{rr}$  on the basis formed by the eigenvectors of  $\mathbf{F}$ , and  $a_n^{(fr)}$  and  $a_n^{(ff)}$  the corresponding matrix elements of  $\mathbf{A}_{fr}$  and  $\mathbf{A}_{ff}$ , respectively. This expression tells us what the eigenvalues of  $\mathbf{F}$  should be. Because  $\mathbf{A}_{rr}$  is positive semidefinite per definition, we have  $a_n^{(rr)} \geq 0$  and each term in expression (13) is minimal when  $\varphi_n = -a_n^{(fr)}/a_n^{(rr)}$  if  $a_n^{(rr)} > 0$ . If  $a_n^{(rr)} = 0$ , then  $a_n^{(fr)} = 0$  holds as well, because along the corresponding eigenvector of  $\mathbf{F}$  there is no variation in the structures. In that case we take  $\varphi_n = 0$ . The minimum value of  $\chi^2$  is then given by

$$\sum_{n=1}^{N_{\text{coord}}} a_n^{(ff)} - \sum_n \frac{[a_n^{(fr)}]^2}{a_n^{(rr)}}, \quad (14)$$

where the second summation extends over the eigenvalues  $\varphi_n \neq 0$ . This expression tells us how to choose the  $N_{\text{dof}}$  eigenvalues of  $\mathbf{F}$  different from zero that give the smallest  $\chi^2$ . We should take the  $N_{\text{dof}}$  components  $n$  with the largest values for  $[a_n^{(fr)}]^2/a_n^{(rr)}$  if  $a_n^{(rr)} \neq 0$  and set  $\varphi_n = -a_n^{(fr)}/a_n^{(rr)}$ . For all other  $n$  we should set  $\varphi_n = 0$ . Because of numerical errors, we will never find that  $a_n^{(rr)} = 0$  holds exactly. We therefore regularize  $[a_n^{(fr)}]^2/a_n^{(rr)}$  by replacing it by

$$\frac{[a_n^{(fr)}]^2 a_n^{(rr)}}{[a_n^{(rr)}]^2 + \epsilon^2}, \quad (15)$$

with  $\epsilon$  a number small with respect to the largest of the values  $a_n^{(rr)}$ .

So far we have only determined the eigenvalues of  $\mathbf{F}$ . The harder problem is to find the eigenvectors. We have found that the following iterative algorithm works best. From expression (9) we get

$$\frac{\partial \chi^2}{\partial F_{kl}} = [\mathbf{F} \mathbf{A}_{rr} + \mathbf{A}_{rr} \mathbf{F} + 2\mathbf{A}_{fr}^T]_{kl}. \quad (16)$$

Suppose we have an approximation  $\tilde{\mathbf{F}}$  of  $\mathbf{F}$ ; then, we do the following. Minimize  $\chi^2$  for  $\tilde{\mathbf{F}} + \lambda[\tilde{\mathbf{F}} \mathbf{A}_{rr} + \mathbf{A}_{rr} \tilde{\mathbf{F}} + \mathbf{A}_{fr} + \mathbf{A}_{fr}^T]$  as a function of  $\lambda$ . The expression in square brackets is the symmetrized version of  $\partial \chi^2 / \partial F_{kl}$ . This is a minimization along a line in the space of all symmetric force-constant matrices. This gives us a new approximation for  $\mathbf{F}$ , but one with a rank that may be larger than  $N_{\text{dof}}$ . We therefore determine the eigenvectors of this new approximation and compute corresponding eigenvalues using (14). This gives us a new approximation  $\tilde{\mathbf{F}}$  that does have a rank smaller or equal than  $N_{\text{dof}}$ . This whole procedure has been repeated until convergence. Appendix B shows two ways to obtain an initial guess for  $\mathbf{F}$ .

### C. Determining the subspace dimension

The procedure above enables us to determine  $\mathbf{F}$  for a given  $N_{\text{dof}}$ . We now need a criterion to determine  $N_{\text{dof}}$ . Simply increasing  $N_{\text{dof}}$  will lead to smaller values of  $\chi^2$ , but this

may be meaningless when the decrease in  $\chi^2$  is only caused by a better fit of the noise in the data; i.e., we are overfitting [6]. The simplest way to deal with the problem is to determine the vibrations for various values of  $N_{\text{dof}}$  and look for a value that gives stable results; i.e., increasing or decreasing  $N_{\text{dof}}$  from that value should not change the vibrations substantially.

Another approach is to use cross validation. We partition all structures in groups  $\{G_k\}$ . We then fit the PES to the structures in  $G_k^{(c)}$ , where  $G_k^{(c)}$  consists of all structures except those in  $G_k$ . We use this fit to predict the forces for the structures in  $G_k$ . We do this for all groups  $G_k$  and use the error estimate

$$\chi_{\text{LMO}}^2 = \frac{1}{N_{\text{coord}} N_{\text{struct}}} \sum_{\alpha=1}^{N_{\text{struct}}} |\mathbf{f}_{\alpha}^{(\text{pred})} - \mathbf{f}_{\alpha}|^2, \quad (17)$$

where  $\mathbf{f}_m^{(\text{pred})}$  is the predicted force based on the fit of the structures in  $G_k^{(c)}$  if structure  $m$  is in group  $G_k$ . This error estimate is called the leave-many-out (cross-validation) error or, if the groups each consist of a single structure, the leave-one-out error [6]. If we look at how  $\chi_{\text{LMO}}^2$  changes with  $N_{\text{dof}}$ , we see that it first decreases, but then flattens out or even increases whereas  $\chi^2$  of Eq. (4) keeps decreasing. This can be interpreted as an indication of overfitting.

The exact value of  $N_{\text{dof}}$  where  $\chi_{\text{LMO}}^2$  has a minimum or where it flattens out is not always easy to determine. Moreover, this value will depend on how the groups are chosen and the precise values of the errors in the forces. (We put the structures in groups randomly, but try to make the groups of the same size.) We use  $\chi_{\text{LMO}}^2$  therefore only as an indicator of overfitting. We also use another indicator, which is a small change to Eq. (4). Instead of dividing by the number of data, we divide by the number of data minus the number of parameters in the fit. This difference can be regarded as the number of degrees of freedom in the fit and leads to the standard residual deviation

$$\chi_{\text{SRD}}^2 = \frac{1}{N_{\text{struct}} N_{\text{coord}} - N_{\text{par}}} \sum_{\alpha=1}^{N_{\text{struct}}} |\mathbf{f}(\mathbf{r}_{\alpha}) - \mathbf{f}_{\alpha}|^2. \quad (18)$$

The second term in the denominator is the number of parameters in Eq. (3) with a force-constant matrix of rank  $N_{\text{dof}}$ . The number of parameters in this matrix can be computed by realizing that for each eigenvector with a nonzero eigenvalue one needs  $N_{\text{coord}} - m$  parameters, with  $m$  the number of restrictions due to the fact that the eigenvector should be normalized and orthogonal to the other eigenvectors. Each nonzero eigenvalue is another parameter determining  $\mathbf{F}$ , and there are  $N_{\text{coord}}$  parameters in  $\mathbf{g}$ . So in total there are  $N_{\text{par}} = N_{\text{coord}} + N_{\text{dof}} + \sum_{m=1}^{N_{\text{dof}}} (N_{\text{coord}} - m) = N_{\text{coord}} + N_{\text{dof}}(2N_{\text{coord}} - N_{\text{dof}} + 1)/2$  parameters to specify the PES. The error estimate  $\chi_{\text{SRD}}^2$  will always increase for large  $N_{\text{dof}}$ , because the denominator decreases with  $N_{\text{dof}}$  whereas the summation will converge to  $N_{\text{coord}} N_{\text{struct}} \chi^2$ .

The third approach we have followed to determine  $N_{\text{dof}}$  is to compute error estimates of the vibrational frequencies using a Monte Carlo simulation [4]. The vibrations should not be sensitive to the exact values of the forces  $f_{\alpha,n}$ . After we

have fitted the PES by minimizing  $\chi^2$  for a certain  $N_{\text{dof}}$ ; we repeat the procedure several times, but with  $f_{\alpha,n} + N(\sqrt{\chi^2})$  instead of  $f_{\alpha,n}$ , where  $N(\sqrt{\chi^2})$  is a random number from a normal distribution centered at 0 and with a width  $\sqrt{\chi^2}$ . If there are vibrations that change a lot, then we may be overfitting.

#### D. Determining the vibrations

Once the force-constant matrix  $\mathbf{F}$  is known, the vibrations follow from the dynamical matrix [3]

$$D_{kl} = \frac{F_{kl}}{\sqrt{m_k m_l}}, \quad (19)$$

with  $m_k$  and  $m_l$  the masses of the atoms with coordinates  $k$  and  $l$ , respectively. The eigenvalues of  $\mathbf{D}$  are the squares of the (angular) vibrational frequencies, and the eigenvectors give the directions in which the atoms move when vibrating.

A nonlinear molecule will have six vibrations with zero frequency. They correspond to three overall translations and three overall rotations. A system that is periodic in three directions will have only three zero-frequency translations corresponding to overall translations. Because our PES varies only in a subspace of the whole configuration space and is assumed to be flat in directions perpendicular to this subspace, we will find many more vibrations with zero frequency. One might therefore be tempted to restrict the calculation of the vibrations to the subspace in which the PES varies. This is, however, not a good idea. The reason is that the vibrational displacements are orthogonal in the usual Euclidean sense only in mass-weighted coordinates, whereas the eigenvectors of the force-constant matrix are orthogonal in normal Cartesian coordinates. Restricting the calculations to the subspace in which the PES varies forces an incorrect orthogonality condition on the eigenvectors of the dynamical matrix. In particular, one gets vibrations that change the center of mass and for molecules also the moments of inertia.

### III. ILLUSTRATIVE EXAMPLES

In this section we present some examples to show the advantages and shortcomings of determining vibrations from geometry optimization data. All examples are taken from our work on molecules adsorbed on surfaces of transition metal catalysts. Vibrational spectroscopy is often used for these systems to determine the adsorption site and geometry, as the vibrations of the adsorbate depend on where and how it binds to the catalyst. Although one is interested in the adsorbate vibrations, there can be a coupling to the substrate vibrations. If one follows the usual method to determine the vibrations, there is the question of how many substrate atoms to include. One would like to include as few substrate atoms as possible, but fixing too many substrate atoms may give incorrect vibrations. We will see that our method automatically includes the appropriate substrate atoms, because these are also the atoms that move when the geometry of the system is optimized.

All our electronic structure calculations were done with the VASP code [7]. This is a program that does density-functional-theory (DFT) calculations of periodic systems. It

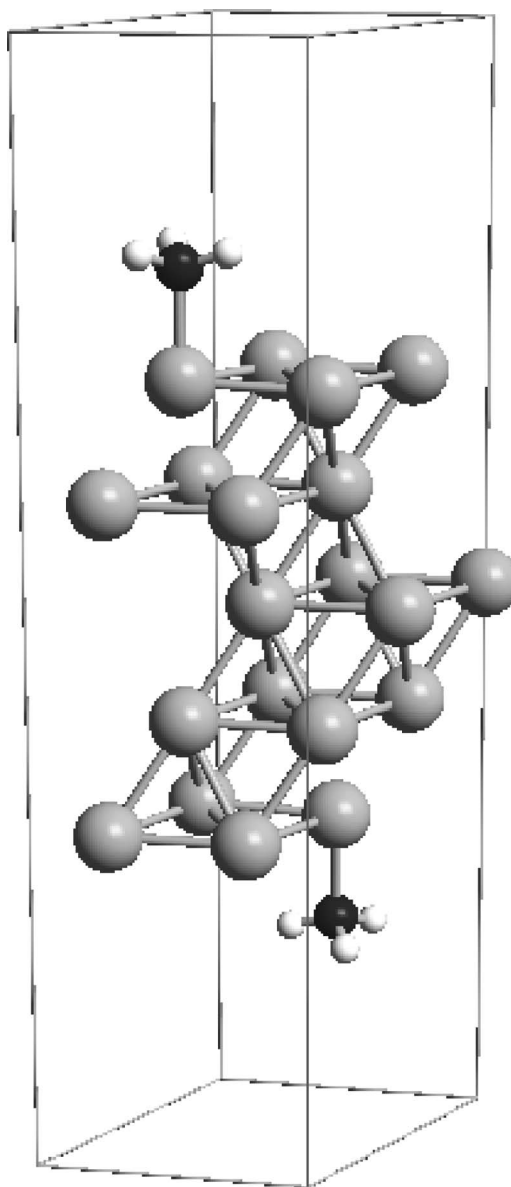


FIG. 1. Supercell used in the DFT calculation of  $\text{NH}_3$  on  $\text{Pt}(111)$ . This cell is periodically repeated in all three directions.

solves the Kohn-Sham equations with a plane-wave basis set and the (relativistic) ultrasoft pseudopotentials introduced by Vanderbilt [8] and generated by Kresse and Hafner [9]. The generalized gradient approximation of Perdew and Wang (PW-91) has been used, because it generally yields good bond energies and vibrations [10]. The code typically gives energies and forces for each structure, but not the force-constant matrix.

Our first example is  $\text{NH}_3/\text{Pt}(111)$ . All calculations on this system were done with a surface model consisting of a supercell with a slab of five metal layers separated by five metal layers replaced by vacuum and a  $2 \times 2$  unit cell.  $\text{NH}_3$  molecules were adsorbed on both sides of the slab, yielding structures with  $S_2$  symmetry to avoid dipole interactions between slabs (see Fig. 1). A  $5 \times 5 \times 1$  grid for Brillouin zone sampling obtained via the Monkhorst package was used and a cutoff of 400 eV. This yielded adsorption energies per

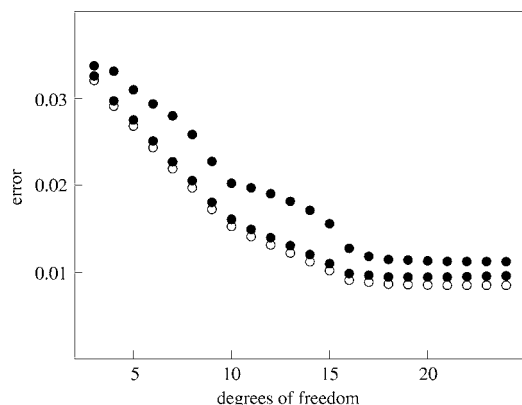


FIG. 2. The leave-many-out error  $\sqrt{\chi_{\text{LMO}}^2}$  (upper solid circles), the standard residual deviation  $\sqrt{\chi_{\text{SRD}}^2}$  (lower solid circles), and the root-mean-square deviation  $\sqrt{\chi^2}$  (open circles) for the fit of the PES for  $\text{NH}_3/\text{Pt}(111)$  as a function of the number of degrees of freedom. All errors are given in  $\text{eV}/\text{\AA}$ . For  $\sqrt{\chi_{\text{LMO}}^2}$  the structures were partitioned randomly into three groups.

adsorbate converged to within 5 kJ/mol with respect to  $k$ -point sampling, energy cutoff, number of slab and vacuum layers, and cell size. The  $\text{NH}_3$  molecules adsorb on top positions with a binding energy of  $-68$  kJ/mol [11]. The geometry optimization yielded 98 different structures that all were used to fit the PES.

Figure 2 shows how the different error estimates  $\chi^2$ ,  $\chi_{\text{LMO}}^2$ , and  $\chi_{\text{SRD}}^2$  change with an increasing number of degrees of freedom in the PES. The root-mean-square deviation  $\chi^2$  decreases monotonically as expected. The leave-many-out error  $\chi_{\text{LMO}}^2$  decreases as well, but its behavior is more erratic. Up until  $N_{\text{dof}}=16$  there is a clear decrease, but after that there is no significant decrease. Ideally, the  $\chi_{\text{LMO}}^2$  should have a minimum, but it is hard to specify exactly where that is. Especially, if we realize that the precise value  $\chi_{\text{LMO}}^2$  depends on how the structures were partitioned into groups, it is even hard to say if there is a minimum at all. The standard residual deviation  $\chi_{\text{SRD}}^2$  resembles  $\chi^2$ , but because of the different denominator, its value increases for large  $N_{\text{dof}}$ . Consequently, it has a minimum, which is in this case at  $N_{\text{dof}}=19$ .

The different error estimates show that for  $N_{\text{dof}}$  between 16 and 19 the fit of the PES does not improve substantially and that we start overfitting. To see what this means we computed the PES's for an even larger range of different numbers of degrees of freedom and calculated for each the vibrations. Figure 3 shows the results. The figure distinguishes between vibrations that vary only little when we change the PES using the Monte Carlo method mentioned in Sec. II C and those that vary a lot. The former have typically errors between 5 and 20  $\text{cm}^{-1}$ , whereas the latter typically have errors larger than 100  $\text{cm}^{-1}$ . As there are also a few vibrations with errors between 20 and 100  $\text{cm}^{-1}$  we take as a dividing line somewhat arbitrarily 50  $\text{cm}^{-1}$ . Apart from the difference in the error estimates of the vibrations, these vibrations also differ in how they vary with the number of degrees of freedom in the PES. The vibrations with small errors vary hardly at all with  $N_{\text{dof}}$ , but that is not the case for the other vibrations. This means that the choice of  $N_{\text{dof}}$  is not critical, if one only looks at the vibrations with small error

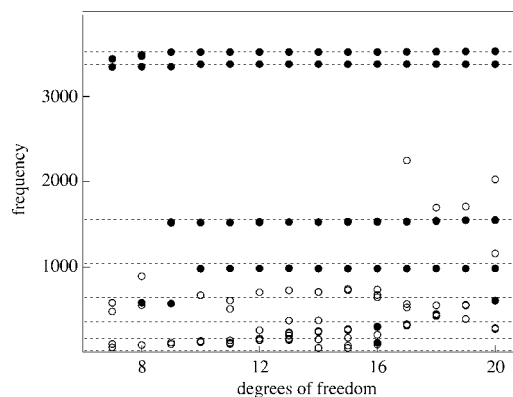


FIG. 3. The vibrational frequencies (in  $\text{cm}^{-1}$ ) as a function of the number of degrees of freedom of the potential-energy surface. Solid circles depict vibrations with small error estimates, open circles with large estimates (see text). The horizontal dashed lines indicate the vibrational frequencies determined with a normal frequency calculation; those at 3528, 1554, 642, and 163  $\text{cm}^{-1}$  are twofold degenerate [11].

estimates and that the method to determine these vibrations is very robust. Nevertheless, overfitting the PES should be avoided. A too large value of  $N_{\text{dof}}$  results in larger values for the error estimates of the vibrational frequencies, and it may result in spurious vibrations that can be hard to distinguish from the real vibrations. In this example this starts happening at  $N_{\text{dof}}=17$  when there is suddenly a vibration with a frequency of about 26 000  $\text{cm}^{-1}$ . This is a clear indication of overfitting, but we have found in other systems that spurious vibrations do not always have such unusual frequencies.

The vibrations that are determined best are also the most important ones: the asymmetric stretches (at  $3525 \pm 5$  and  $3522 \pm 6$   $\text{cm}^{-1}$  for  $N_{\text{dof}}=16$ ), the symmetric stretch (at  $3381 \pm 5$   $\text{cm}^{-1}$ ), the scissor modes (at  $1534 \pm 14$  and  $1526 \pm 13$   $\text{cm}^{-1}$ ), and the umbrella mode (at  $978 \pm 12$   $\text{cm}^{-1}$ ). These values should be compared to values that are obtained with a normal frequency calculation, which yields 3529, 3528, 3376, 1555, 1552, and 1040  $\text{cm}^{-1}$ , respectively [11]. The agreement is excellent, especially considering that the latter took more than 2 processor weeks on the a PC with 1600 MHz AMD 242 Opteron processors, whereas the former took only a few minutes on a PC with a single 1800-MHz AMP processor. Of course, the latter calculation also yielded the other vibrations of the adsorbate.

We note that the higher frequencies have smaller errors. An explanation for this observation is the following. The errors in the forces are probably similar for all forces. Because frequencies depend on the square root of the forces, the errors in the frequencies are *inversely* proportional the square root of the forces; because  $\omega = \sqrt{f/m}$ , a change in the force  $f \rightarrow f + \Delta f$  causes a change in the frequency  $\omega \rightarrow \omega + \Delta\omega$  with  $\Delta\omega = \Delta f \sqrt{1/4mf}$ .

Our second example is  $\text{NO}/\text{Pt}(111)$ . Maybe even more useful than the determination of vibrational frequencies is our method for the verification of transition states. Transition-state searches regularly end in higher-order saddle points. It is therefore necessary to determine the number of negative eigenvalues of the force-constant matrix, or the

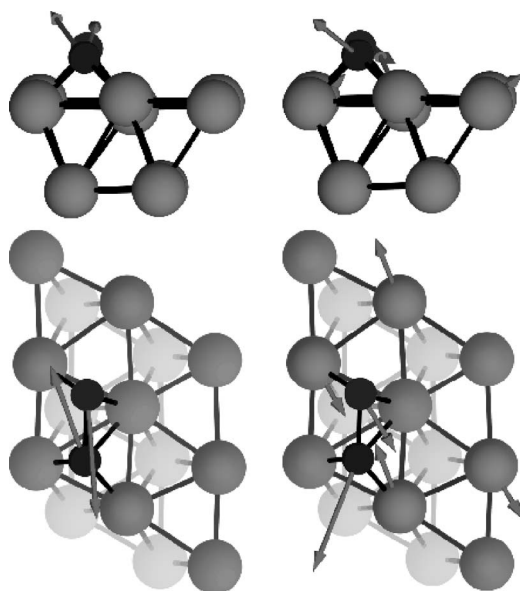


FIG. 4. A candidate transition state for NO dissociation on Pt(111). Both figures show the same structure, but the arrows indicate different normal modes with imaginary frequencies  $i426\text{ cm}^{-1}$  on the left and  $i132\text{ cm}^{-1}$  on the right. The large spheres are Pt atoms. The darker small sphere is the N atom. The other small sphere is the O atom.

number of imaginary frequencies. A transition state should have only one. The normal procedure is to do a normal-mode analysis for the structure corresponding to the candidate transition state. Instead, we suggest to employ the method of this paper.

The method cannot prove that a certain structure is a transition state. It may not find all imaginary frequencies. So if it finds no or only one imaginary frequency, it may still mean that we have a higher-order saddle point. If it finds two or more imaginary frequencies, however, we can exclude the possibility of a transition state, and we use the eigenvectors corresponding to the negative eigenvalues of the force-constant matrix to find a better candidate. We have found that our method is actually quite reliable as far as the number of imaginary frequencies is concerned, even though it provides no certainty. We think that this is caused by the fact that the methods for finding a transition state approach the transition state from lower energies and consequently sample the directions of the negative eigenvalues of the force-constant matrix quite well.

To illustrate the method for transition states we will discuss the dissociation of NO on Pt(111) [11]. The computational details are the same as for  $\text{NH}_3/\text{Pt}(111)$  above. The transition-state search consisted of the nudged-elastic-band method to get an approximate structure [12] and the quasi-Newton method for fine-tuning [13]. NO preferentially adsorbs on fcc sites, and when it dissociates the N atom stays at that site whereas the O atom moves to another fcc site nearby. We have found two possible transition states for this process. In the correct transition state the atoms are already the same distance apart as in the final state, but they are both at bridge site. Figure 4 shows the other candidate transition state. Table I gives the frequencies and their error estimates.

TABLE I. Frequencies of a candidate transition state for NO dissociation on Pt(111). Error estimates calculated as described at the end of Sec. II C are less than  $2\text{ cm}^{-1}$  for all frequencies.

Method	Frequencies (in $\text{cm}^{-1}$ )
This paper	612, 460, 331, 289, 190, 182, 176, 171, 168, 159, 152, 150, 140, 137, 132, 122, 111, 108, 105, 100, 95, 92, 86, 84, 78, 75, 69, 60, 58, 54, 48, 42, 34, 29, 15, $i132$ , $i426$
Finite difference	612, 460, 329, 290, 180, 160, 148, 144, 102, 86, 79, 74, 63, 59, 39, 29, $i127$ , $i431$

As the transition state was particularly hard to find, the transition-state search methods yielded no less than 307 structures near the candidate transition state. From this we could determine in total 37 frequencies. This number is the number of degrees of freedom for which  $\chi_{\text{SRD}}^2$  is minimal. As all errors are quite small, it seems that in this case many more frequencies can be determined than for the case of  $\text{NH}_3/\text{Pt}(111)$ . This is probably due to the large number of structures.

We also see that two frequencies are imaginary. This indicates that we have a higher-order saddle point. (Because the errors are small, it seems very unlikely that either of these vibrations are spurious.) The corresponding eigenvectors of the dynamical matrix show that the vibration at  $i426\text{ cm}^{-1}$  has the atoms move in opposite directions, whereas the vibration at  $i132\text{ cm}^{-1}$  has them moving almost parallel. Because the latter does not change the N-O distance, it seems likely that this does not correspond to the reaction coordinate. We therefore distorted the system in the direction of this eigenvector and started another transition-state search. This gave us the proper transition state described above. Both our method and the usual finite-difference method gave just one imaginary frequency for the corresponding structure.

The two examples above are taken from two projects on the reduction and oxidation of  $\text{NH}_3$ . In these projects we have used our method to compute vibrations from geometry optimizations in many other cases; we have looked at different adsorbates ( $\text{NH}_x$ ,  $\text{OH}_y$ , N, O, H) that can adsorb on different sites (top, bridge, fcc, hcp) of different surfaces [Pt(111), Pt(112), Rh(111)], at initial states of reactions with many combinations of coadsorbed species, and at the transition states of all reactions. For the most important adsorption structures and reactions we have compared the results of our method with the results from the finite-difference method. In all cases where we did this the agreement between the two was as good as the agreement in the two examples above. This suggests that our method is quite reliable and for complicated reaction systems like ours very useful.

#### IV. CONCLUSIONS

We have shown here a method to compute harmonic vibrations that uses the structures and the forces that are

obtained from a geometry optimization. Compared to the normal procedure that is used in conjunction with a DFT calculation, which uses a finite-difference scheme, the method here has the main advantage that it is much faster. (We often find speed ups of three or four orders of magnitude.) The reason for this is that it does not require additional electronic structure calculations. Instead it does very inexpensive fits. In addition it does not require a good determination of the stationary point of the potential-energy surface; such a point is a result of the method. The main drawback of the method is that it does not guarantee any particular vibration. Because it is so fast, however, little is lost when it does not give satisfactory results. One can always use other methods in such a situation. The method includes several checks to determine the reliability of its results, but it seems to be quite robust.

The particular vibrations that one can determine with the method of this paper depend on the structures that are generated during the geometry optimization. These need not have much to do with the vibrations. So there is an element of arbitrariness involved. If we want to have information on particular vibrations, then we can try to influence the geometry optimization by starting with a structure that is distorted according to the vibrations that we are interested in. In principle, it should be possible in this way to obtain all vibrations of a system. Whether this is then still more efficient than using the normal finite differencing is not clear.

We have applied the method mainly to vibrations of small molecules adsorbed on transition metal surfaces and to the verification of transition states of such molecules. The method seems to work very well for such systems. The reason is that geometry optimization and transition-state searches of such systems lead to many different structures, the relevant vibrations include only a few degrees of freedom, and the potential-energy surface along those few degrees of freedom is sampled quite well. Other systems with this characteristic should also be good candidates for the method.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: AN ALTERNATIVE APPROACH TO DETERMINE THE FORCE-CONSTANT MATRIX

We can write the force-constant matrix with rank  $F \leq N_{\text{dof}}$  as

$$\mathbf{F} = \mathbf{U}\Phi\mathbf{U}^T, \quad (\text{A1})$$

where  $\Phi$  is a diagonal matrix of dimension  $N_{\text{dof}}$  and  $\mathbf{U}$  is a  $N_{\text{dof}} \times N_{\text{coord}}$  matrix with columns that are orthonormal.  $\Phi$

contains the eigenvalues and  $\mathbf{U}$  the eigenvectors of  $\mathbf{F}$ . The matrix  $\Phi$  can be determined as described following Eq. (14). Here we discuss two other ways to determine  $\mathbf{U}$ .

One way is to regard  $\chi^2$  in Eq. (9) as a function of the matrix elements of  $\mathbf{U}$  and use a standard minimization routine to determine  $\mathbf{U}$ . Because we have the restriction of orthonormality of the columns, we cannot work with  $\mathbf{U}$  directly in such a routine. We therefore write  $\mathbf{U} = \exp(\mathbf{X})$ , where  $\mathbf{X}$  is an antisymmetric matrix;  $\mathbf{X}^T = -\mathbf{X}$ . With  $\mathbf{X}\mathbf{V} = i\mathbf{V}\Omega$ ,  $\Omega$  real and diagonal, and  $\mathbf{V}^{-1} = \mathbf{V}^T$  we have  $\mathbf{U} = \mathbf{V} \exp(i\Omega)\mathbf{V}^T$ . This shows how to compute  $\mathbf{U}$  from  $\mathbf{X}$ . The advantage of  $\mathbf{X}$  is that we can just take the matrix elements of the upper-right part without being bothered by any restrictions. So we minimize  $\chi^2$  as a function of  $\mathbf{X}$ . It turns out that this works, but unless  $N_{\text{dof}}$  is very small (less than 10), this approach appears to be very time consuming.

Another way to determine  $\mathbf{U}$  might be the following. The derivative of  $\chi^2$  with respect to  $\mathbf{U}$  is given by

$$\frac{\partial \chi^2}{\partial U_{kl}} = 2[\Phi\mathbf{U}^T(\mathbf{F}\mathbf{A}_{rr} + \mathbf{A}_{rr}\mathbf{F})]_{kl}. \quad (\text{A2})$$

Together with the restriction on the orthonormality of the columns of  $\mathbf{U}$ , which can be taken into account using Lagrange multipliers, this gives an expression that determines  $\mathbf{U}$ . Unfortunately, we were not able to find a method to solve this expression.

#### APPENDIX B: APPROXIMATIONS TO THE FORCE-CONSTANT MATRIX

To start the iterative procedure to determine the force-constant matrix as described following Eq. (16), we need a first approximation for the matrix. One way to obtain such an approximation is to assume some set of eigenvectors and calculate the eigenvalues according to the procedure described following Eq. (14). We have found that one good set of eigenvectors can be obtained by diagonalizing  $\mathbf{A}_{fr}\mathbf{A}_{rr}^{-1}\mathbf{A}_{fr}^T$  as the eigenvalues of this matrix appear to approximate the terms  $[a_n^{(fr)}]^2/a_n^{(rr)}$  in Eq. (14) well.

Alternatively we can get a closed expression for the matrix  $\mathbf{F}$  if we weaken the restriction on its form. If we only require that  $\mathbf{F}$  be symmetric, then we can minimize  $\chi^2$ . The symmetrized derivative of  $\chi^2$  with respect to the matrix elements of  $\mathbf{F}$  has been shown in Sec. II B to be  $\mathbf{F}\mathbf{A}_{rr} + \mathbf{A}_{rr}\mathbf{F} + \mathbf{A}_{fr} + \mathbf{A}_{fr}^T$ . This should be equal to  $\mathbf{0}$ . With

$$\mathbf{A}_{rr}\mathbf{E} = \mathbf{E}\Lambda \quad (\text{B1})$$

and  $\mathbf{E}$  orthogonal and  $\Lambda$  diagonal we get

$$\mathbf{E}^T\mathbf{F}\mathbf{E}\Lambda + \Lambda\mathbf{E}^T\mathbf{F}\mathbf{E} = -\mathbf{E}^T(\mathbf{A}_{fr} + \mathbf{A}_{fr}^T)\mathbf{E}. \quad (\text{B2})$$

Taking matrix element  $(n, m)$  this becomes

$$(\Lambda_{nn} + \Lambda_{mm})(\mathbf{E}^T\mathbf{F}\mathbf{E})_{nm} = -[(\mathbf{E}^T\mathbf{A}_{fr}\mathbf{E})_{nm} + (\mathbf{E}^T\mathbf{A}_{fr}\mathbf{E})_{mn}], \quad (\text{B3})$$

or

$$(\mathbf{E}^T\mathbf{F}\mathbf{E})_{nm} = -\frac{(\mathbf{E}^T\mathbf{A}_{fr}\mathbf{E})_{nm} + (\mathbf{E}^T\mathbf{A}_{fr}\mathbf{E})_{mn}}{\Lambda_{nn} + \Lambda_{mm}}. \quad (\text{B4})$$



Because  $\mathbf{A}_{rr}$  is often singular, this expression can lead to numerical problems. One might think that the whole problem should be solved in the subspace of the range of  $\mathbf{A}_{rr}$ , but that does not lead to the best force-constant matrix. In particular we get  $(\mathbf{E}^T \mathbf{F} \mathbf{E})_{nm} = 0$  if  $\Lambda_{nm} = 0$  or  $\Lambda_{mm} = 0$ , whereas when one really only wants  $(\mathbf{E}^T \mathbf{F} \mathbf{E})_{nm} = 0$  if  $\Lambda_{nm} = 0$  and  $\Lambda_{mm} = 0$ . This can be accomplished by regularization of Eq. (B4); i.e., we use

$$(\mathbf{E}^T \mathbf{F} \mathbf{E})_{nm} = - \frac{[(\mathbf{E}^T \mathbf{A}_{fr} \mathbf{E})_{nm} + (\mathbf{E}^T \mathbf{A}_{fr} \mathbf{E})_{mn}][\Lambda_{nn} + \Lambda_{mm}]}{[\Lambda_{nn} + \Lambda_{mm}]^2 + \epsilon^2}, \quad (\text{B5})$$

with  $\epsilon$  a number small with respect to the largest eigenvalues of  $\mathbf{A}_{rr}$ .

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