Ab Initio Theory of NMR Chemical Shifts in Solids and Liquids

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We present a theory for the *ab initio* computation of NMR chemical shifts (σ) in condensed matter systems, using periodic boundary conditions. Our approach can be applied to periodic systems such as crystals, surfaces, or polymers and, with a supercell technique, to nonperiodic systems such as amorphous materials, liquids, or solids with defects. We have computed the hydrogen σ for a set of free molecules, for an ionic crystal LiH, and for a H-bonded crystal HF, using density functional theory in the local density approximation. The results are in excellent agreement with experimental data. [S0031-9007(96)01901-1]

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Nuclear magnetic resonance (NMR) is one of the most widely used experimental techniques in structural chemistry. In particular, the chemical shift (σ) spectra are a fingerprint of the molecular geometry and the chemical structure of the material under study. Although the interpretation of these spectra generally relies on empirical rules, *ab initio* calculations of σ for molecules have led in many cases to an unambiguous determination of the microscopic structure [1]. So far, *ab initio* calculations of σ have been restricted to finite systems such as isolated molecules or clusters [2,3]. This is a serious limitation, because most of the NMR experiments are performed on liquid samples. Moreover, it is now possible to measure σ also in solids with the resolution required for structural determinations [4,5]. E.g., σ spectra have been used for the characterization of amorphous carbon [6]. In this Letter, we present a formalism to compute, from first principles, σ in extended systems using periodic boundary conditions. Our approach can be applied to periodic systems such as crystals, surfaces, or polymers and, using a supercell technique, to nonperiodic systems such as amorphous materials, liquids, or solids with defects. In the case of the amorphous solid or liquid, the atomic coordinates may be generated by *ab initio* molecular dynamic simulations [7,8].

The chemical shift measures the local magnetic field in a sample induced by a uniform applied magnetic field. The computation of σ in an extended system is not straightforward, since the expectation values of the individual terms of the perturbative Hamiltonian for extended eigenstates are not well-defined quantities [9]. To overcome this problem, we follow Ref. [10] in which a theory for the computation of the macroscopic magnetic susceptibility is presented. In particular, (i) we obtain the magnetic response to a uniform field as the long-wave limit of a periodic field, and (ii) we use a generalized f-sum rule to remove the numerical instability which occurs in this limit. We apply the resulting equations to real systems, describing the electronic structure within density functional theory (DFT) in the local density approximation (LDA). We compute the hydrogen σ for a set of small molecules, for an ionic crystal, and for a H-bonded crystal. Our results are in excellent agreement with experimental data.

A uniform, external magnetic field $\mathbf{B}_{\mathrm{ext}}$, applied to a sample induces an electronic current density $\mathbf{J}_{\mathrm{in}}(\mathbf{r})$. This current produces an induced magnetic field $\mathbf{B}_{\mathrm{in}}(\mathbf{r})$. If $\mathbf{B}_{\mathrm{ext}}$ is small enough, a condition realized in NMR experiments, then

$$\mathbf{B}_{\mathrm{in}}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}_{\mathrm{ext}} \, . \tag{1}$$

Here $\overleftrightarrow{\sigma}(\mathbf{r})$ is the chemical shift tensor. With NMR spectroscopy, it is possible to measure the symmetric part of $\overleftrightarrow{\sigma}(\mathbf{r})$, or more often its trace, $\sigma(\mathbf{r}) = (1/3)\mathrm{Tr}[\overleftrightarrow{\sigma}(\mathbf{r})]$, at the position of the nonzero spin nuclei.

In the bulk of a periodic system, $\overleftrightarrow{\sigma}(\mathbf{r})$ is also periodic. We may write

$$\overleftrightarrow{\sigma}(\mathbf{r}) = \sum_{\mathbf{G}} \overleftrightarrow{\tilde{\sigma}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{2}$$

where $\mathbf{G}$ are the reciprocal lattice vectors. For $\mathbf{G} \neq \mathbf{0}$, $\overleftrightarrow{\tilde{\sigma}}(\mathbf{G})$ is a bulk property,

$$\overleftrightarrow{\tilde{\sigma}}(\mathbf{G}) = -4\pi\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0}) \, , \tag{3}$$

where $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{G}')$ is the magnetic susceptibility matrix. However, for $\mathbf{G} = \mathbf{0}$, $\overleftrightarrow{\tilde{\sigma}}(\mathbf{0})$ is *not* a bulk property. Its value depends on the shape of the sample, and is determined by macroscopic magnetostatics. In our calculations we assume a spherical sample, for which

$$\overleftrightarrow{\tilde{\sigma}}(\mathbf{0}) = -\frac{8\pi}{3}\overleftrightarrow{\chi}(\mathbf{0},\mathbf{0}) \, , \tag{4}$$

where $\overleftrightarrow{\chi}(\mathbf{0},\mathbf{0})$ is the macroscopic susceptibility [11]. Thus the calculation of σ in a periodic system requires the knowledge of $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})$. We compute the macroscopic susceptibility $\overleftrightarrow{\chi}(\mathbf{0},\mathbf{0})$ following Ref. [10]. The other elements of $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})$ are computed as described below.

The susceptibility matrix is defined as the second derivative of the total energy with respect to the external magnetic field. In particular,

$$\hat{\mathbf{b}}_{-\mathbf{G}} \cdot \overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})\hat{\mathbf{b}}_{\mathbf{0}} = -\frac{\partial^2 E[\mathbf{B}]}{\partial B_{\mathbf{0}}\partial B_{-\mathbf{G}}}\bigg|_{\mathbf{B}=0} = -E''_{\mathbf{0},-\mathbf{G}} \, , \tag{5}$$

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where $E[\mathbf{B}]$ is the total energy of the system per unit volume in the external magnetic field $\mathbf{B}(\mathbf{r})$, $\mathbf{B}(\mathbf{r}) = [B_{\mathbf{0}}\hat{\mathbf{b}}_{\mathbf{0}} + B_{-\mathbf{G}}\hat{\mathbf{b}}_{-\mathbf{G}}\exp(-i\mathbf{G}\cdot\mathbf{r})]$, and $\hat{\mathbf{b}}_{-\mathbf{G}}$ and $\hat{\mathbf{b}}_{\mathbf{0}}$ are vectors of unit length. Thus $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})$ can be evaluated using perturbation theory. However, the expectation values of the perturbative Hamiltonians for a uniform field between extended eigenstates are ill defined. To avoid this problem, we modulate the external periodic field with a finite wave vector $\mathbf{q}$, $\mathbf{B}(\mathbf{r}) = \{B_{\mathbf{q}}\hat{\mathbf{b}}_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}) + B_{-\mathbf{G}-\mathbf{q}}\hat{\mathbf{b}}_{-\mathbf{G}-\mathbf{q}}\exp[-i(\mathbf{G}+\mathbf{q})\cdot\mathbf{r}]\}$ [12], and we recover the results for the uniform field by considering the limit [10]:

$$\hat{\mathbf{b}}_{-\mathbf{G}}\cdot\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})\hat{\mathbf{b}}_{\mathbf{0}} = -\lim_{q\to 0} E''_{\mathbf{q},-\mathbf{G}-\mathbf{q}}\,. \tag{6}$$

We now consider a spin compensated system described by a single particle Hamiltonian. The derivatives of the Hamiltonian required to compute $E''_{\mathbf{q},-\mathbf{G}-\mathbf{q}}$ are

$$\begin{aligned} H'_{\mathbf{q}} &= \frac{-i}{2}\left(e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{a}_{\mathbf{q}}\cdot\nabla + \mathbf{a}_{\mathbf{q}}\cdot\nabla e^{i\mathbf{q}\cdot\mathbf{r}}\right), \\ H'_{-\mathbf{G}-\mathbf{q}} &= \frac{-i}{2}\left(e^{-i(\mathbf{G}+\mathbf{q})\cdot\mathbf{r}}\mathbf{a}_{-\mathbf{G}-\mathbf{q}}\cdot\nabla + \mathbf{a}_{-\mathbf{G}-\mathbf{q}}\cdot\nabla e^{-i(\mathbf{G}+\mathbf{q})\cdot\mathbf{r}}\right), \quad H''_{\mathbf{q},-\mathbf{G}-\mathbf{q}} = \mathbf{a}_{\mathbf{q}}\cdot\mathbf{a}_{-\mathbf{G}-\mathbf{q}}e^{-i\mathbf{G}\cdot\mathbf{r}}\,, \end{aligned} \tag{7}$$

where $\mathbf{a}_{\mathbf{s}} = (i\mathbf{s}\times\hat{\mathbf{b}}_{\mathbf{s}})/(cs^2)$, and c is the speed of light. Using perturbation theory we obtain

$$\begin{aligned} E''_{\mathbf{q},-\mathbf{G}-\mathbf{q}} &= f(\mathbf{a}_{\mathbf{q}},\mathbf{a}_{-\mathbf{G}-\mathbf{q}},\mathbf{G},\mathbf{q}) \\ &\quad + 2\mathbf{a}_{\mathbf{q}}\cdot\mathbf{a}_{-\mathbf{G}-\mathbf{q}}\int\frac{d^3k}{(2\pi)^3} \\ &\quad \times\sum_{i\in\mathcal{O}}\langle u_{\mathbf{k},i}|e^{-i\mathbf{G}\cdot\mathbf{r}}|u_{\mathbf{k},i}\rangle\,, \end{aligned} \tag{8}$$

where $|u_{\mathbf{k},i}\rangle$ is the periodic part of the Bloch eigenstate of the unperturbed Hamiltonian $H_{\mathbf{k}}$ with eigenvalue $\epsilon_{\mathbf{k},i}$, $\mathcal{O}$ are the sets of occupied bands, and

$$\begin{aligned} f(\mathbf{a}_1,\mathbf{a}_2,\mathbf{G},\mathbf{q}) = \int d^3r[&h(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r},\mathbf{q}) \\ &+ h^*(\mathbf{a}_1^*,\mathbf{a}_2^*,\mathbf{r},-\mathbf{q})]e^{-i\mathbf{G}\cdot\mathbf{r}}, \end{aligned} \tag{9}$$

where the integral is performed in the periodic cell, with

$$\begin{aligned} &h(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r},\mathbf{q}) \\ &= \int\frac{d^3k}{(2\pi)^3}\sum_{i\in\mathcal{O}}[\langle u_{\mathbf{k},i}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{a}_2\cdot(-i\nabla+\mathbf{k}+\mathbf{q})|u_{\mathbf{k},i}^{\mathbf{q},\mathbf{a}_1}\rangle \\ &\quad + \langle u_{\mathbf{k},i}|\mathbf{a}_2\cdot(-i\nabla+\mathbf{k})|\mathbf{r}\rangle\langle\mathbf{r}|u_{\mathbf{k},i}^{\mathbf{q},\mathbf{a}_1}\rangle]\,. \end{aligned} \tag{10}$$

$|u_{\mathbf{k},i}^{\mathbf{q},\mathbf{a}_1}\rangle$ is the first order change of the eigenstate $|u_{\mathbf{k},i}\rangle$ due to a field with wave vector $\mathbf{q}$. It can be obtained by solving the linear system

$$\begin{aligned} &(\epsilon_{\mathbf{k},i} - H_{\mathbf{k}+\mathbf{q}})|u_{\mathbf{k},i}^{\mathbf{q},\mathbf{a}_1}\rangle \\ &\quad = Q_{\mathbf{k}+\mathbf{q}}\mathbf{a}_1\cdot(-i\nabla+\mathbf{k}+\mathbf{q}/2)|u_{\mathbf{k},i}\rangle\,, \end{aligned} \tag{11}$$

where $Q_{\mathbf{k}+\mathbf{q}} = (1 - \sum_{i\in\mathcal{O}}|u_{\mathbf{k}+\mathbf{q},i}\rangle\langle u_{\mathbf{k}+\mathbf{q},i}|)$ is the projector onto the empty subspace.

The first term on the right-hand side of Eq. (8) is obtained as a second order perturbation with the first order derivatives of the Hamiltonian $H'_{\mathbf{q}}$ and $H'_{-\mathbf{G}-\mathbf{q}}$. The second term in the right-hand side of Eq. (8) is obtained as a first order perturbation with the second order derivative of the Hamiltonian $H''_{\mathbf{q},-\mathbf{G}-\mathbf{q}}$. Since $\mathbf{a}_{\mathbf{q}}$ diverges as $1/q$ for $q\to 0$, the two terms on the right-hand side of Eq. (8) individually diverge as $1/q$. To remove this divergence, which would produce a numerical instability, we use the generalized f-sum rule,

$$\begin{aligned} 2\mathbf{a}_1\cdot\mathbf{a}_2\int\frac{d^3k}{(2\pi)^3}&\sum_{i\in\mathcal{O}}\langle u_{\mathbf{k},i}|e^{-i\mathbf{G}\cdot\mathbf{r}}|u_{\mathbf{k},i}\rangle \\ &= -f(\mathbf{a}_1,\mathbf{a}_2,\mathbf{G},\mathbf{0})\,. \end{aligned} \tag{12}$$

Substituting the f-sum rule into Eq. (8), we obtain $E''_{\mathbf{q},-\mathbf{G}-\mathbf{q}} = [f(\mathbf{a}_{\mathbf{q}},\mathbf{a}_{-\mathbf{G}-\mathbf{q}},\mathbf{G},\mathbf{q}) - f(\mathbf{a}_{\mathbf{q}},\mathbf{a}_{-\mathbf{G}-\mathbf{q}},\mathbf{G},\mathbf{0})]$. Then, for $\mathbf{G}\neq\mathbf{0}$,

$$\begin{aligned} \hat{\mathbf{b}}_{-\mathbf{G}}\cdot\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})\hat{\mathbf{b}}_{\mathbf{0}} &= -\lim_{q\to 0}E''_{\mathbf{q},-\mathbf{G}-\mathbf{q}} = -\frac{\partial}{c^2G^2\partial q} \\ &\quad\times f(\hat{\mathbf{q}}\times\hat{\mathbf{b}}_{\mathbf{0}},\mathbf{G}\times\hat{\mathbf{b}}_{-\mathbf{G}},\mathbf{G},q\hat{\mathbf{q}})|_{q=0}\,, \end{aligned} \tag{13}$$

where $\hat{\mathbf{q}}$ is the unit vector in the direction of $\mathbf{q}$. Finally, the derivative with respect to q in Eq. (13) can also be evaluated using the following limit:

$$\hat{\mathbf{b}}_{-\mathbf{G}}\cdot\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})\hat{\mathbf{b}}_{\mathbf{0}} = -\lim_{q\to 0}[f(\hat{\mathbf{q}}\times\hat{\mathbf{b}}_{\mathbf{0}},\mathbf{G}\times\hat{\mathbf{b}}_{-\mathbf{G}},\mathbf{G},q\hat{\mathbf{q}}) - f(\hat{\mathbf{q}}\times\hat{\mathbf{b}}_{\mathbf{0}},\mathbf{G}\times\hat{\mathbf{b}}_{-\mathbf{G}},\mathbf{G},-q\hat{\mathbf{q}})]/(2qc^2G^2)\,. \tag{14}$$

Note that, for $\mathbf{G}\neq\mathbf{0}$, $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})$ is proportional to the first derivative of f with respect to q, whereas the macroscopic susceptibility $\overleftrightarrow{\chi}(\mathbf{0},\mathbf{0})$ is proportional to the second derivative of f with respect to q [10].

In practice, we evaluate numerically $\overleftrightarrow{\chi}(\mathbf{G},\mathbf{0})$ using Eq. (14) with a small, but finite q, and the $\mathbf{k}$ integral in Eq. (10) with a finite summation in the irreducible wedge of the Brillouin zone.

We describe the electrons using DFT-LDA; i.e., we neglect any explicit dependence of the exchange-correlation functional (E_{xc}) on the current density. The current dependence of E_{xc} could be taken into account using the approximate functional proposed in Ref. [13], but, in practice, this produces only negligible corrections to σ in real systems [3]. An *ad hoc* procedure to include many-body effects beyond DFT in the calculation of σ has been proposed in [14]. While this approach improves over DFT in small molecules, the corrections to DFT vanish for periodic systems, where the eigenstates are always extended. In general, to compute the second order variation in the DFT total energy with respect to an external perturbation, one should take into account the linear variation of the Hamiltonian induced by the linear variation of the charge $\delta\rho$. However, if the perturbation is a magnetic field, $\delta\rho$ is zero by time reversal symmetry. Thus Eqs. (7)–(14) are correct within DFT.

In the present calculation, we will consider the magnetic response of valence electrons only. We describe the ionic cores by norm conserving pseudopotentials [15] in the Kleinman-Bylander form [16]. This approximation does not affect σ of the nuclei without core electrons, such as H [2,17], but those containing core electrons. In the latter case, σ computed with pseudopotentials differs from the one computed with an all-electron scheme by three different terms: (i) the diamagnetic core contribution, which is independent of the chemical environment; (ii) a contribution due to the transitions from valence states to core states [10]; (iii) a contribution due to the difference between the all-electron valence wave functions and the pseudo-wave-functions in the core region. We found that, for first row atoms such as carbon, the error due to the pseudopotential is minor, since the terms (ii) and (iii) are usually much smaller than the range of variation of σ with the chemical environment. In the present paper, however, we present only the results for σ of H, which is not affected by the use of pseudopotentials. Finally, in our pseudopotential calculation, we replace $(-i\nabla + \mathbf{k} + \mathbf{q}/2)$ in Eq. (11) with $(\mathbf{v}^p_{\mathbf{k}} + \mathbf{v}^p_{\mathbf{k}+\mathbf{q}})/2$, where $\mathbf{v}^p_{\mathbf{k}} = (d/d\mathbf{k})H^p_{\mathbf{k}}$ is the velocity operator, and $H^p_{\mathbf{k}}$ is the pseudo-Hamiltonian [18].

We expand the wave functions using a plane wave (PW) basis set. We obtain $|u^{\mathbf{q},\mathbf{a}_1}_{\mathbf{k},i}\rangle$ by solving Eq. (11) with a conjugate gradient minimization [19]; i.e., we never use the unoccupied eigenstates of $H^p_{\mathbf{k}}$. We obtain $f(\mathbf{a}_1, \mathbf{a}_2, \mathbf{G}, \mathbf{q})$ from $|u^{\mathbf{q},\mathbf{a}_1}_{\mathbf{k},i}\rangle$ using fast Fourier transforms. Thus, the computational effort to evaluate σ for all nuclei in the sample is comparable to that required for a computation of the total energy [20]. We compute σ in systems containing atoms of H, C, Li, and F. For H we use a local pseudopotential to speed up the convergence with respect to the PW basis [21]. For C, Li, and F atoms, we use a pseudopotential with a nonlocal s projector to describe the interaction of valence states with the 1s core states. We use a PW energy cutoff of 100 Ry for the F atom, and of 70 Ry for the other atoms. Molecular and crystalline structures are taken from experiments [22]. The results for the free molecules are obtained using supercells, such that the error on σ due to interaction between a molecule and its periodic replica is smaller than 0.1 parts per million (ppm).

TABLE I. Computed and measured H chemical shifts (σ) for a set of free molecules.

	σ theory (ppm)	σ experiment (ppm)
H_2	25.9	26.2[a]
CH_4	30.7	30.61[a]
C_2H_6	29.7	29.86[b]
C_2H_4	24.5	25.43[b]
C_2H_2	28.6	29.26[b]

[a] Reference [23].

[b] Reference [24].

The results for a set of molecules are reported in Table I. All the computed values are in excellent agreement with experimental data. The discrepancies are larger for C_2H_4 and C_2H_2, in which a double and a triple C-C bond exist, respectively. This could indicate a relatively larger inaccuracy of LDA in describing these types of bonds. Similar agreement with experiments for the hydrogen σ in molecules is found in previous calculations [2,3].

The results for molecular and crystalline LiH are reported in Table II. LiH is an ionic system, which crystallizes in the rock-salt structure. The Li-H equilibrium distance in the crystal is significantly larger than that of the molecule. Our results show that the difference between σ in the molecule and in the solid is very small. To verify if σ is sensitive to the geometry, we consider a crystal at a pressure of 65 GPa, in which the Li-H distance is equal to that of the molecule. In this case, we find a much larger value of σ. Thus, σ of the crystal and of the free molecule are only similar at the equilibrium geometries.

The results for molecular and crystalline HF are reported in Table III. The intramolecular bond of HF is covalent. In the liquid and solid phases, the HF molecules are bonded together in zigzag chains via H bonds. HF has the strongest H bonding found in nature. This strong intermolecular bond is reflected in the large variation of σ observed in the transition from the gas phase to the liquid phase, and in the large temperature dependence of σ in the liquid phase [23]. The HF crystal is constituted of a 2D stacking of parallel 1D zigzag chains. We compute σ for the crystal at the experimental geometries measured for a DF crystal at two temperatures, 4.2 and 85 K [25]. The computed σ in the free HF molecule is in outstanding agreement with experimental data. In the crystal, the computed σ decreases dramatically to a value close to the

TABLE II. Computed H chemical shifts (σ) in LiH for a free molecule and a spherical crystalline sample (in the rock-salt structure). d_0 is the equilibrium bond length of the molecule, a is the lattice constant, and a_0 is the experimental equilibrium lattice constant. For $a = 2d_0$, the shortest Li-H distance in the crystal is equal to d_0.

		σ theory (ppm)
LiH molecule	$d_0 = 1.595$	26.6
LiH crystal	$a = a_0 = 4.08$	26.3
LiH crystal	$a = 2d_0 = 3.19$	31.2

TABLE III. Computed and measured hydrogen chemical shifts σ in HF for a free molecule, a spherical crystalline sample, and a spherical liquid sample. T is the temperature.

	T (K)	σ theory (ppm)	σ experiment (ppm)
HF molecule		28.4	28.5[a]
HF crystal	4.2	20.71	
HF crystal	85	21.76	
HF liquid	214		21.45[b]

[a] Reference [23].
[b] Reference [24].

one measured in the liquid phase (we are not aware of any experimental measurement of σ for solid HF). Also the theoretical variation of σ with temperature, $\delta\sigma/\delta T = 0.013$ ppm/K, is very close to the one measured in the liquid, which is $d\sigma/dT = 0.0135$ ppm/K [23]. Thus, with respect to σ, the behavior of the solid is very similar to that of the liquid. Interestingly, a single H bond does not account for the large decrease of σ observed in the condensed phases. Indeed, the computed σ for the central H atom in a HF-HF dimer, is closer to the σ of the free molecule than to that of the liquid [2].

In conclusion, we have presented an *ab initio* theory for the evaluation of NMR chemical shifts (σ) in extended systems. We have computed, for the first time, σ in real solids. Our results show that DFT-LDA predicts hydrogen σ which are in excellent agreement with experiment. The evaluation of σ requires the same numerical effort as the computation of the total energy [20]. Thus, our approach can be applied to supercells containing up to a hundred atoms, which are sufficient to model liquids or amorphous materials [6–8].

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[21] We verified that the values for Hσ obtained with the H pseudopotential are rigidly shifted by -0.3 ppm with respect to the values obtained without the H pseudopotential. The results reported in the present paper have been corrected for this effect.
[22] H_2: $r_{\mathrm{HH}} = 0.767$ Å; CH_4: $r_{\mathrm{CH}} = 1.094$ Å; C_2H_6: $r_{\mathrm{CH}} = 1.096$ Å, $r_{\mathrm{CC}} = 1.532$ Å, $\theta_{\mathrm{CCH}} = 111.5°$; C_2H_4: $r_{\mathrm{CH}} = 1.103$ Å, $r_{\mathrm{CC}} = 1.337$ Å, $\theta_{\mathrm{CCH}} = 121.4°$; C_2H_2: $r_{\mathrm{CH}} = 1.061$ Å, $r_{\mathrm{CC}} = 1.206$ Å; HF (molecule): $r_{\mathrm{HF}} = 0.926$ Å.
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