

# Quantization of the dipole moment and of the end charges in push-pull polymers

Konstantin N. Kudin<sup>a)</sup> and Roberto Car

Department of Chemistry and Princeton Institute for Science, and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey 08544, USA

Raffaele Resta

CNR-INFN DEMOCRITOS National Simulation Center, Via Beirut 2, I-34014 Trieste, Italy and Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

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A theorem for end-charge quantization in quasi-one-dimensional stereoregular chains is formulated and proved. It is a direct analog of the well-known theorem for surface charges in physics. The theorem states the following: (1) Regardless of the end groups, in stereoregular oligomers with a centrosymmetric bulk, the end charges can only be a multiple of  $1/2$  and the longitudinal dipole moment per monomer  $p$  can only be a multiple of  $1/2$  times the unit length  $a$  in the limit of long chains. (2) In oligomers with a noncentrosymmetric bulk, the end charges can assume any value set by the nature of the bulk. Nonetheless, by modifying the end groups, one can only change the end charge by an integer and the dipole moment  $p$  by an integer multiple of the unit length  $a$ . (3) When the entire bulk part of the system is modified, the end charges may change in an arbitrary way; however, if upon such a modification the system remains centrosymmetric, the end charges can only change by multiples of  $1/2$  as a direct consequence of (1). The above statements imply that—in all cases—the end charges are uniquely determined, *modulo an integer*, by a property of the bulk alone. The theorem's origin is a robust topological phenomenon related to the Berry phase. The effects of the quantization are first demonstrated in toy LiF chains and then in a series of *trans*-polyacetylene oligomers with neutral and charge-transfer end groups. © 2007 American Institute of Physics. [DOI: 10.1063/1.2799514]

## I. INTRODUCTION

Push-pull polymers have received much attention due to their highly nonlinear electronic and optical responses. Such molecules usually contain a chain of atoms forming a conjugated  $\pi$ -electron system with electron donor and acceptor groups at the opposite ends. Upon an electronic excitation a charge is transferred from the donor to the acceptor group, leading to remarkable nonlinear properties. What is surprising, however, is that—as will be shown in the present work—nontrivial features already appear when addressing the lowest-order response of such molecules to the static electric fields, i.e., their dipole moment. A model push-pull polymer is shown in Fig. 1. Note that instead of addressing computationally challenging excited states, we would rather much prefer to focus on the ground state properties. Therefore, in the case of the push-pull system shown in Fig. 1, we simulate the charge transfer not by moving an electron but by moving a proton from the COOH to NH<sub>2</sub> groups located at the opposite ends.

The most general system addressed here is, therefore, a long polymeric chain, which is translationally periodic (stereoregular, alias “crystalline”) along, say, the  $z$  direction, with period  $a$ . We are considering *insulating* chains only, i.e., chains where the highest occupied molecular orbital–lowest unoccupied molecular orbital gap stays finite in the long-

chain limit. The chain is terminated in an arbitrary way, possibly with some functional group attached, at each of the two ends. In the case of a push-pull polymer, such groups are a donor-acceptor pair. Therefore, the most general system is comprised of  $N_c$  identical monomers (“crystal cells”) in the central (“bulk”) region, augmented by the left- and right-end groups. If the total length is  $L$ , the bulk region has a length

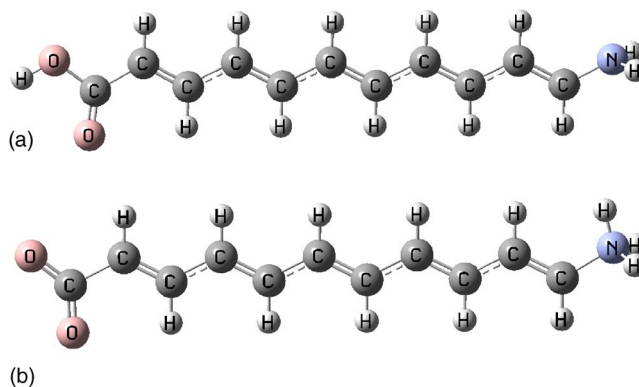


FIG. 1. (Color online) Two states of a prototypical push-pull system. The long insulating chain of alternant polyacetylene has a “donor” (NH<sub>2</sub>) and “acceptor” (COOH) groups attached at the opposite ends. The charge transfer occurring in such systems upon some physical or chemical process is simulated here by moving a proton from the COOH to NH<sub>2</sub> groups: in (a) we show the “neutral” structure and in (b) the “charge-transfer” one. The two structures share the same “bulk,” where the cell (or repeating monomer) is C<sub>2</sub>H<sub>2</sub>, and the figure is drawn for  $N_c=5$ .

<sup>a)</sup>Electronic mail: kkudin@princeton.edu

$L_c = N_c a$ , and the two end regions together account for a length  $L - L_c$ , which is given once and for all, and independent of  $N_c$ . Indeed, Fig. 1 is a typical realization of such a system.

Here, we consider the large  $N_c$  limit of some physical properties for “long” polymeric chains. For instance, the leading term in the energy is linear in  $N_c$ ; hence, the energy per cell (or per monomer) goes to a finite limit. This owes to the fact that the bulk region is extensive in size (i.e., proportional to  $N_c$  and to  $L_c$ ), while the end regions are nonextensive. When studying the large  $N_c$  limit of such systems with a one particle method, with either the Hartree-Fock (HF) or density-functional-theory (DFT) approaches, it is quite convenient to exploit translational symmetry by addressing infinite chains, where the HF canonical orbitals, as well as the Kohn-Sham (KS) orbitals, assume the Bloch form. Well established methods, algorithms, and computer codes<sup>1-6</sup> provide, for example, the energy per cell in this case. When comparing it to the real finite system, the effects of the termination are irrelevant to the leading order in  $N_c$ .

The central quantity in the present work is the longitudinal dipole moment  $d$  of our generic system. In the chain orientation adopted earlier, this longitudinal moment is simply the  $z$  component of the total dipole. Even this property is extensive; hence, in the large-system limit, it is more appropriate to consider the dipole per unit cell  $p = d/N_c$ ; in view of the nonextensive character of the end effects, and that  $L = aN_c$ , we equivalently have  $p = ad/L$ . We draw attention to a semantic issue: despite using the symbol  $p$ , we carefully avoid throughout this work using the word “polarization.” This is because in solid-state physics, polarization means the dipole moment per cell, while in quantum chemistry (QC), it is sometimes used in a different sense.

The dipole moment of any finite system is a very simple quantity. In fact, its electronic contribution is simply the first moment of the electron density, which is obviously well-defined for any bound state, whose density vanishes exponentially at infinity. We notice that if we address instead an infinite periodic system, where the single-particle orbitals have the Bloch form, the first moment of the density becomes ill defined, and the dipole needs quite a different treatment than in finite systems. The ultimate solution of this long-standing problem came in the 1990s, with the advent of the modern theory of polarization, based on a Berry phase.<sup>7-10</sup>

In this work, we investigate long but finite polymeric chains such as the push-pull polymer in Fig. 1, using the standard QC approach. In particular, we consider the longitudinal dipole  $p$  and the end charges  $Q_{\text{end}}$  of such systems. The main message of the present work is that the end charges, and the corresponding dipole of long polymeric chains, are quantized. Such quantization may look counter-intuitive, being in sharp contrast with what happens in small molecules, where the dipole is *not quantized* and can assume any value.

To the best of the authors’ knowledge, the quantization discussed here seems to be quite novel in the QC literature and in the theory of polymers at large. Nonetheless, the analogous phenomenon is well established in the physics of

surfaces, where it goes under the name of “quantization of the surface charge.” It appeared for the first time in a 1966 paper by Heine<sup>11</sup> and was discussed by several authors afterward.<sup>12</sup> A rather complete account can be found in a 1986 paper by Niu,<sup>13</sup> whereas the relationships between the quantization of the surface charge and the modern theory of polarization are discussed in Ref. 8. A closely related theorem concerns the quantization of charge transport.<sup>14,15</sup>

The novelty of the present work in relation to the solid-state physics literature is two-fold. First, the theorem is specialized to polymers and presented within the standard QC language and notation. Second, the proof of the theorem is based on quite different concepts and methods from, for example, Ref. 13.

The paper is organized as follows. In Sec. II, we state the quantization theorem. Immediately after, in Sec. III, we report a set of *ab initio* HF calculations for a toy LiF chain where all the features of the theorem can be heuristically observed. Next, in Sec. IV, we prove the theorem within the framework of a one particle approach in several steps: by mapping the finite and infinite quantum systems onto an equivalent system of point charges, by relating such finite and infinite systems to each other, and then by considering the most general finite system with arbitrary end groups. Finally, in the last part of Sec. IV, we outline the path that could be followed in order to prove the theorem for a case of a correlated wave function method (i.e., beyond the single-particle level). In Sec. V, we demonstrate how the theorem manifests itself in the case of realistic insulating *trans*-polyacetylene oligomers shown in Fig. 1. The final section is devoted to our conclusions, while the appendix discusses an approach to visualize the end charges by a sliding-window convolution.

## II. STATEMENT OF THE QUANTIZATION THEOREM

The quantization theorem is most intuitive when formulated in terms of the net *charges* present (or absent) at the two ends of our (overall charge-neutral) linear chain. We *define* the net end charges as

$$d = Q_{\text{end}} L, \quad (1)$$

i.e., as point charges that, when located at the end points of a classical neutral rod of length  $L$ , would produce the same total dipole  $d$  as the real quantum system. Since, in the large-system limit, we have

$$d = p N_c = p \frac{L}{a}, \quad (2)$$

in the same limit, we also have

$$Q_{\text{end}} = \pm \frac{p}{a}. \quad (3)$$

Thus, the dipole moment per cell  $p$  behaves identically to  $Q_{\text{end}}$  multiplied by the unit-cell length  $a$ .

The quantization theorem<sup>13</sup> can then be stated as follows. (1) Whenever the bulk of the chain is centrosymmetric, the end charges  $Q_{\text{end}}$  can only be an integer multiple of  $1/2$  (in a.u.), irrespective of the terminations of the chain. By

attaching functional groups at the chain ends, the end charges can only change by an integer (if the bulk is unchanged). (2) Whenever the bulk is *not centrosymmetric*, the end charges  $Q_{\text{end}}$  may assume any value which nonetheless is set by the nature of the bulk. By attaching any functional groups at the chain ends, such value can only change by an integer (again if the bulk is unchanged). (3) Finally, if we modify the bulk of the system, by changing either the Hamiltonian or the character of the wave function,  $Q_{\text{end}}$  may change by an arbitrary amount. However, in the special case where we modify the bulk of a centrosymmetric system, while preserving this symmetry,  $Q_{\text{end}}$  may only change by an integer multiple of  $1/2$ , as a direct consequence of (1). The above statements imply that—in all cases—the end charges are uniquely determined, *modulo an integer*, by a property of the bulk alone.

The quantization rules have a topological character and are, therefore, extremely robust;<sup>16</sup> however, they become exact only asymptotically, in the large-system limit. This is especially true for quasi-one-dimensional (quasi-1D) systems where, due to the long ranged electrostatics, the convergence of many physical properties to their asymptotic value is polynomial, such as was demonstrated for the longitudinal polarizability in Ref. 17.

### III. A TOY MODEL: 1D BINARY CHAIN

For pedagogical purposes, we consider finite binary chains of atoms of chemical species A and B, with a two-atom cell of constant length  $a$ , schematized in Fig. 2. To illustrate various realizations of the quantization theorem, we adopt three different geometries shown in Fig. 2: (a) the bulk is centrosymmetric and all nearest-neighbor distances are equal to  $a/2$  and [(b) and (c)] the bulk is noncentrosymmetric and the nearest-neighbor distances are alternatively equal to  $a/2 + \delta$  and  $a/2 - \delta$ .

If the atoms A and B are of the same chemical species, the bulk is centrosymmetric in all cases: hence, as anticipated, we expect the end charges  $Q_{\text{end}}$  to be an integer multiple of  $1/2$ . Furthermore, since the whole finite system is centrosymmetric, its dipole and the end charges  $Q_{\text{end}}$  vanish. This is indeed a very trivial realization of the quantization theorem.

Instead, for an ionic system, such as LiF, we would expect on chemical intuition that the system would be predominantly ionic for reasonable values of  $a$  and predominantly nonionic at large  $a$  values (given that it dissociates into neutral atoms). We performed the HF calculations for such systems with  $N_c$  up to 65. Owing to the double-occupancy constraint, restricted HF (RHF) calculations converge to an ionic

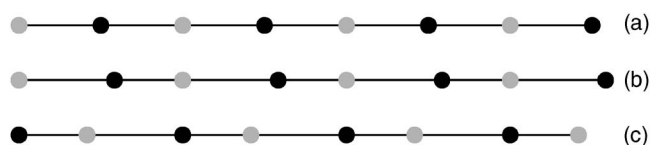


FIG. 2. Simple binary chains, where four monomer units are shown. (a) centrosymmetric bulk and [(b) and (c)] noncentrosymmetric bulk. Notice that (b) and (c) share the same bulk but have different terminations. We have actually run RHF and UHF calculations for such chains, choosing F as the gray atom and Li as the black atom, at variable sizes  $N_c$ .

ground state for any  $a$  value. To allow for nonionic configuration, it is then useful to also approach the problem at the unrestricted HF (UHF) level. The calculations were carried out with GAUSSIAN 03.<sup>6</sup> Given the qualitative purpose of the calculations, a small STO-3G basis set was fully adequate.

For the sake of clarity, we keep  $a$  fixed (equal to 10 a.u.) throughout: in fact, in this way, we unambiguously detect the changes in the dipole and the end charges as the system switches between the two states. In essence, the UHF method allows us to vary the electronic structure of the bulk itself. We note that to obtain consistent differences, we ran UHF calculations in the specific high-spin configuration, with one unpaired electron per atom. The UHF wavefunctions were carefully constructed in such a way that the unpaired electron on *every* F atom always resided on the  $p$  orbital oriented along the chain.

We indicate by  $d(N_c)$  the dipole of a chain of  $N_c$  cells; the asymptotic value of  $p$  is then defined as

$$p = \lim_{N_c \rightarrow \infty} \frac{d(N_c)}{N_c} = \lim_{N_c \rightarrow \infty} [d(N_c) - d(N_c - 1)]. \quad (4)$$

When dealing with finite-size chains, we will use the notation

$$p(N_c) = d(N_c) - d(N_c - 1). \quad (5)$$

Our results are summarized in Fig. 3 and discussed below.

We first address the centrosymmetric case, shown in Fig. 2(a). For the ionic, i.e., RHF case, we compute  $p(65) = 4.9997$ . Alternatively, using the asymptotic relationship  $Q_{\text{end}} = p/a$ , we get end charges of  $\pm 1/2$ , as required by the quantization theorem stated in Sec. II, to an accuracy of  $2.5 \times 10^{-5}$ . This result happens to be identical to a classical system of  $\pm 1$  point charges, located at the nuclear sites. It is then tempting to attribute this result to the strongly ionic nature of the system; however, this would be incorrect because the quantization is a robust topological phenomenon,<sup>16</sup> which occurs in systems of *any ionicity*. The very small de-

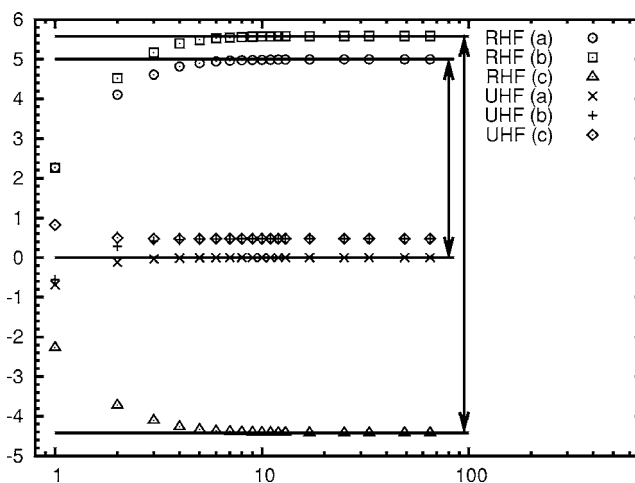


FIG. 3. Longitudinal dipole moment per cell  $p(N_c)$ , defined in Eq. (5), of the LiF chain as a function of  $N_c$ . The labels (a), (b), and (c) refer to the geometries schematized in Fig. 2. The short double arrow indicates the half-quantum difference of 5 a.u. between the RHF and the UHF for the centrosymmetric system (a); the long double arrow indicates 1 quantum difference of 10 a.u. between RHF calculations for systems (b) and (c).

viation ( $2.5 \times 10^{-5}$ ) found here is a finite-size error and *not an effect* of partial ionicity.

When, for the same geometry, we run the high-spin UHF calculations, we get instead  $p(65) = 7.0 \times 10^{-7}$  or equivalently  $Q_{\text{end}} = 0$ , again in agreement with the quantization theorem, with a finite-size error of  $7.0 \times 10^{-8}$ . This seems to indicate neutrality atom by atom but is instead, again, a robust quantization phenomenon. In fact—as shown below—the end charges in the corresponding noncentrosymmetric cases (b) and (c) are rather small but *nonzero*. In both RHF and UHF cases, the end charges  $Q_{\text{end}}$  are an integer multiple of  $1/2$ , in agreement with the theorem for the case where the bulk of the chain is centrosymmetric.

The theorem also states that, by attaching any group at the two ends, the end charges may only change by an integer. A simple realization can be obtained by starting from Fig. 2(a) and attaching two additional atoms at the ends: a black atom (Li) on the left and a gray atom (F) on the right. Clearly, the dipole reverses the sign and the end charges exchange between themselves, in fact, varying by  $\pm 1$ . However, owing to the quantization theorem, the quantized result is general and holds for *any* (nonextensive) *modification* performed at the chain ends.

At this point we notice that a similar robustness (with respect to changes in both ionicity and chain terminations) was heuristically noticed earlier in the QC literature. In particular, this effect was noticed in the Hückel-Hamiltonian calculations of Ref. 18, but no rationale was given for it.

Next, we move on to analyze the noncentrosymmetric cases, Figs. 2(b) and 2(c), where we have chosen alternating nearest-neighbor distances of 4.75 and 5.25 a.u. Since the bulk of the chain is noncentrosymmetric, the asymptotic dipole per cell  $p$  may assume any value. In fact, we find, from the RHF calculations,  $p(65) = 5.5826$  in case (b) and  $p(65) = -4.4170$  in case (c). However, since the two chains share the same bulk, the quantization theorem states that their asymptotic  $p$  value may only differ by an integer times  $a$ . Actually, at  $N_c = 65$ , the computed difference is 9.9995 (shown in Fig. 3 by the bigger double arrow). This corresponds to a change in  $Q_{\text{end}}$  of 1, with a finite-size error of  $5.0 \times 10^{-5}$ .

It is worthwhile to compare the above  $p$  values, as computed for our toy quantum system, to the corresponding values for a classical system of  $\pm 1$  point charges located at the atomic sites. Clearly, the geometry of Fig. 2(b) yields  $p = 5.25$ , while the one of Fig. 2(c) yields  $p = -4.75$ . Instead, as mentioned above, the actual values for the quantum calculations are  $p = 5.58$  and  $-4.42$ , respectively. We notice that in both cases, the difference is 1 quantum, which corresponds to the lattice parameter  $a = 10$ . But—at variance with the centrosymmetric case discussed above—the quantum system and the corresponding system of classical point charges have noticeably different dipoles.

In the case of the UHF calculations, cases (b) and (c) differ significantly at small sizes but converge to the same values of  $p = 0.4770$  and  $Q_{\text{end}} = 0.0477$  in the large size limit. This corresponds to a quantized difference equal to 0. Indeed, 0 is one of the quantized values allowed by the theorem for the difference between (b) and (c). We have previ-

ously observed that the UHF calculations result in a nonionic ground state, where the atoms are predominantly neutral. However, rigidly assembling a set of neutral atoms would result in  $Q_{\text{end}} = 0$ , while our asymptotic value is  $Q_{\text{end}} = 0.0477$ . The fact that  $Q_{\text{end}}$  is small though definitely nonzero can be interpreted, on chemical grounds, as a residual ionicity (due to either charge transfer or the induced displacement of the electrons away from the nuclei) in the high-spin UHF state at  $a = 10$ . We point out, once more, the qualitative difference from the corresponding UHF state in the centrosymmetric case (a), where the quantization theorem forces  $Q_{\text{end}}$  to vanish and no residual ionicity is observed.

We note that a somewhat more intuitive way to obtain the end charges  $Q_{\text{end}}$  is by utilizing the sliding-window convolution described in the Appendix. In contrast to the test calculations presented above, such an approach does not actually require the evaluation of the dipole moment as an intermediate step to obtain  $Q_{\text{end}}$ .

## IV. PROOF OF THE QUANTIZATION THEOREM

### A. Mapping the finite quantum system onto a system of classical point charges

We first consider a *finite* quasi-1D oligomer, with nuclei of charges  $Z_s$  at positions  $\mathbf{r}_s = (x_s, y_s, z_s)$ ; let  $N_\sigma$  ( $\sigma = \alpha, \beta$ ) be the number of electrons in each spin channel. The longitudinal component of the total dipole is

$$d = \sum_s Z_s z_s - \sum_\sigma \sum_{j=1}^{N_\sigma} \int d\mathbf{r} z |w_{\sigma j}(\mathbf{r})|^2, \quad (6)$$

where the  $w_{\sigma j}$ 's are single-particle spin orbitals. Since Eq. (6) is invariant with respect to a unitary transformation of the occupied orbitals among themselves, we assume the  $w_{\sigma j}$ 's to be localized spin orbitals. For instance, this could be achieved according to Boys' criterion.<sup>19</sup> This allows us to define the ( $z$ -projected) centers of the electron distribution corresponding to  $w_{\sigma j}$ 's as

$$\bar{z}_{\sigma j} = \int d\mathbf{r} z |w_{\sigma j}(\mathbf{r})|^2. \quad (7)$$

Then, the dipole becomes

$$d = \sum_s Z_s z_s - \sum_\sigma \sum_{j=1}^{N_\sigma} \bar{z}_{\sigma j}. \quad (8)$$

We have, therefore, mapped our finite quantum-mechanical system onto an equivalent system of integer point charges. Notice that each of the two terms in Eq. (8) depends on the choice of the origin, while their sum provides an origin-independent, unambiguous dipole value. Overall charge neutrality of the system is essential in this respect.

### B. The infinite system

If the quasi-1D system is stereoregular, we may also consider its infinite-length limit, which is periodic with period  $a$  in the  $z$  direction. The spin orbitals (either HF or KS)  $\varphi_{\sigma n k}$  are labeled by a band index  $n$  ( $n \leq N_\sigma$ ) and by a 1D Bloch vector  $k$ . Note that now, we denote by  $N_\sigma$  the number

of electrons in the spin channel *per cell*. The Bloch theorem yields

$$\varphi_{\sigma mk}(\mathbf{r}) = e^{ikz} u_{\sigma mk}(\mathbf{r}), \quad (9)$$

and  $u_{\sigma mk}(\mathbf{r})$  is lattice periodic,

$$u_{\sigma mk}(\mathbf{r}) = u_{\sigma mk}(\mathbf{r} + \mathbf{R}_l), \quad (10)$$

where  $\mathbf{R}_l = (0, 0, la)$ . We normalize the orbitals  $\varphi_{\sigma mk}(\mathbf{r})$  to 1 over the period  $a$  (i.e., over one unit cell).

For an *insulating* infinite chain the localization transformation leads to Wannier orbitals<sup>20,21</sup> of index  $n$  in cell  $l$ ,

$$w_{\sigma ml}(\mathbf{r}) = \frac{a}{2\pi} \int_0^{2\pi/a} dk e^{ikla} \varphi_{\sigma mk}(\mathbf{r}). \quad (11)$$

A well-known identity<sup>22,23</sup> relates the  $z$ -projected center of the Wannier orbitals to the Berry phase as

$$\bar{z}_{\sigma ml} = \int d\mathbf{r} z |w_{\sigma ml}(\mathbf{r})|^2 = \frac{a}{2\pi} \gamma_{\sigma m} + la, \quad (12)$$

where the Berry phase of a band<sup>22</sup> is the real dimensionless number defined as

$$\gamma_{\sigma m} = i \int_0^{2\pi/a} dk \langle u_{\sigma mk} | u'_{\sigma mk} \rangle, \quad (13)$$

where  $u_{\sigma mk}$  is the lattice periodic part of the Bloch orbital from Eq. (9), and the prime denotes the  $k$  derivative.

What is notable about Eq. (12) is that it allows one to map continuous bands to *integer* point charges located at

$$\bar{z}_{\sigma ml} = \frac{a}{2\pi} \gamma_{\sigma m} + la. \quad (14)$$

Then, one can formally define the dipole value for a periodic point-charge system that includes nuclei and localized electrons as

$$p_0 = \sum_s Z_s z_s - \sum_{\sigma} \sum_{n=1}^{N_{\sigma}} \bar{z}_{\sigma nl}. \quad (15)$$

This periodic point-charge model system already has some interesting quantization properties. Specifically, if one were to shift the site of any of the integer point charges (either nuclei or localized electrons) from  $z_i$  to an equivalent lattice point  $z_i + ma$ , the value of the dipole would change from  $p_0$  to  $p$ , with the difference being an integer times  $a$ . Furthermore, such a change is the only possible outcome of any origin shift in a periodic system of integer point charges.

The quantization of the allowed periodic dipole moment values found in a system of integer point charges naturally corresponds to a similar effect in quantum-mechanical systems. In the quantum case, this arbitrariness by an integer multiple of  $a$  stems from the topological character of the issue, and is related to the occurrence of *phases*,<sup>16</sup> (here,  $\gamma_{\sigma m}$ ) which are naturally defined as *modulo*  $2\pi$ . One could try to get rid of this arbitrariness and define a “unique”  $p_0$  value by choosing all the  $z_s$  and  $\bar{z}_{\sigma m0}$  in Eq. (15) to be inside the unit cell, which is indeed the most natural choice. However, the choice of the cell origin in a periodic system is itself necessarily arbitrary. Thus, the quantum arbitrariness is unavoid-

able. In fact, it is easy to realize that different choices for the unit-cell origin yield  $p_0$  values may differ by an integer times  $a$ .

### C. Relating the finite system to the infinite one

Suppose we build a finite chain “cut from the bulk:” i.e., we assemble a finite number  $N_c$  of monomers, each monomer being the unit cell of a corresponding infinite periodic chain. We keep the nuclear geometry of each cell unrelaxed. With such a construction, the finite chain is the exact fragment of the infinite one. The dipole  $d(N_c)$  of this fragment is an extensive, nonarbitrary quantity. The asymptotic dipole per cell  $p$  defined earlier in Eq. (4) is nonarbitrary as well. In contrast, the corresponding dipole per cell  $p_0$  of the periodic infinite system in Eq. (15) has the intrinsic “quantum” arbitrariness discussed above. It is, however, worth observing that, when cutting the fragment from the infinite chain, we need to specify “how to cut,” i.e., how to choose the unit cell of the periodic system.

At this point we can put the finite (though large) fragment with  $N_c$  monomer units and the respective infinite system side by side. We localize the orbitals of the finite system as per Eqs. (6) and (8) according to Boys’<sup>19</sup> criterion, while for the periodic system, we choose the Wannier orbitals  $w_{\sigma ml}$  in Eqs. (11) and (15) according to the Marzari-Vanderbilt<sup>21</sup> (MV) criterion. Boys’ localization transformation can be performed on any finite fragment of any given chain, irrespective of whether the chain becomes insulating or conducting in the infinite- $N_c$  limit. However, in the conducting case, Boys’ orbitals become more delocalized with increasing  $N_c$ ; a precise statement of this fact is that the spherical second moment  $\langle r^2 \rangle - |\langle \mathbf{r} \rangle|^2$  of the Boys-orbital charge distributions, averaged over the number of electrons in the system, *diverges* in the large  $N_c$  limit.<sup>24</sup> In the insulating case, instead, this spherical second moment converges to a finite limit. Notice that the MV criterion is the direct extension of Boys’ one to periodic systems and makes sense in the insulating case only: no Wannier orbitals can be defined in the conducting case. The spherical second moment of the MV-orbital charge distribution averaged over the number of electrons in the cell is finite as well and, in fact, coincides with the large  $N_c$  limit of the same moment for Boys’ orbitals.<sup>24</sup> Furthermore the long-standing conjecture that the localization of the MV orbitals is exponential has finally been proven recently.<sup>25</sup> Due to this need for localizability we have stressed from the very beginning that the present quantization theorem applies to insulating chains only. In this case (and only in this case), the localized orbitals  $w_{\sigma j}$  in the central part of the finite chain will be identical, by construction, to the Wannier orbitals  $w_{\sigma ml}$  of the periodic system, by a suitable mapping of the indices  $\sigma j$  onto their  $\sigma ml$  counterparts.

Addressing next the end regions of the finite system, we notice that Boys’ orbitals will deviate significantly from their Wannier counterparts due to electronic relaxation. However, it is crucial to stress that the central region is *extensive* (length proportional to  $N_c$ ), while the end regions are *nonextensive* (length independent of  $N_c$ , though dependent on the chemical nature of the system).

It is expedient to initially consider an intermediate “frozen” system where, while cutting the fragment, we keep the electronic distribution unrelaxed (in addition to fixed nuclear geometry). By this we mean that we identify the Boys’ orbitals entering the dipole definition [Eq. (6)], with the corresponding Wannier orbitals, *even in the end regions*. This amounts to replacing all the electronic-charge centers  $\bar{z}_{\sigma j}$  in Eq. (8) with the corresponding Wannier centers  $\bar{z}_{\sigma ml}$ . By construction, the dipole  $d(N_c)$  of the frozen finite system is thus exactly equal to  $N_c p_0$  and, therefore,  $p^{(\text{frozen})} \equiv p_0$ .

Next, we relax the electron distribution. This amounts to displacing the electronic-charge centers  $\bar{z}_{\sigma j}$  in Eq. (8), albeit only in the end regions. With no loss of generality, we now focus on a center  $\bar{z}_{\sigma j}$  in the right-end region. Two cases are possible: either (i) a relatively small displacement occurs within the same right-end region or (ii) the center jumps from the right-end region to the left-end one. The center cannot move into the central region because each central cell must remain charge neutral. In case (i), the dipole  $d(N_c)$  changes by a nonextensive amount and therefore,  $p = p^{(\text{frozen})}$ , in the large- $N_c$  limit. In case (ii), the dipole  $d(N_c)$  changes by an extensive amount and it is then easy to realize that the actual  $p$  may only differ from  $p^{(\text{frozen})}$  by an integer times  $a$  (again in the large- $N_c$  limit). Since the number of the available electronic-charge centers  $\bar{z}_{\sigma j}$  in the end regions is, in turn, nonextensive, the electronic relaxation of the finite fragment may only change its dipole per cell from  $p_0$  to  $p_0$  plus an integer times  $a$ .

We remind that  $p_0$  is a bulk property, defined for the periodic infinite chain in terms of Berry phases [Eqs. (12) and (15)]. The key message is, therefore, that the allowed  $p$  (dipole per cell) values of a finite fragment cut from the infinite chain are *not arbitrary*: in fact, in the large- $N_c$  limit, they must be equal to the bulk  $p_0$  value plus an integer times  $a$ . A restatement of the same message is that the end charges  $Q_{\text{end}}$  of the finite fragment must be equal to  $p_0/a$  (a property of the bulk), plus an integer. This “charge rigidity” is a topological property<sup>16</sup> of paramount importance.

## D. The most general case

We are now ready to complete the proof of the main statements given in Sec. II. Here, we include the nuclear relaxation effects and address the case of the most general quasi-1D stereoregular polymer, possibly with functional groups attached to each end, such as the one shown in Fig. 1.

Our system consists of a central region of  $N_c$  monomers, asymptotically identical, augmented with two end regions built with any chemical groups, in arbitrary nuclear configuration. The central region is periodic both in the nuclear coordinates and the electron distribution, and can be thought of as a fragment of an infinite periodic chain. The fundamental assumption is that the infinite chain is insulating, with completely filled one-electron bands. This condition makes the localization procedure possible, which is the central tool in our proof.

All of the previous considerations of Sec. IV C apply to the central region of our most general system. In particular,

the bulk dipole per cell (or per monomer)  $p_0$  is defined as above. We report here its expression for the sake of clarity,

$$p_0 = \sum_s Z_s z_s - \frac{a}{2\pi} \sum_{\sigma} \sum_{n=1}^{N_{\sigma}} \gamma_{\sigma n}, \quad (16)$$

where  $z_s$  are the nuclear coordinates,  $\gamma_{\sigma n}$  are the Berry phases [Eq. (13)], and their  $2\pi$  arbitrariness has been fixed by requiring that the corresponding Wannier centers lie in the unit cell.

In order to complete the proof, it is sufficient to consider the effects of the end groups on the total dipole. This amounts to adding or removing nuclei and Boys’ orbitals in Eq. (6), all in the end regions. From the point of view of Eq. (8), we are thus adding or subtracting nuclear ( $Z_s z_s$ ) and electronic ( $\bar{z}_{\sigma j}$ ) extra terms to the sums, that is, equivalent to adding a set of integer point charges to each of the two end regions, while the system remains overall neutral. Each of these point charges changes the total dipole by a term which is (to leading order in  $N_c$ ) an integer multiple of  $N_c a$ ; hence, the corresponding dipole per cell  $p$  may only vary by an integer times  $a$ . We further notice that the total number of the extra point charges is nonextensive in the large- $N_c$  limit. This completes the proof.

The final statement of the quantization theorem in Sec. II is that in all cases, the end charges are uniquely determined, *modulo an integer*, by a property of the bulk alone. After presenting the proof, we indeed find that the longitudinal dipole per cell  $p$  of the most general fully relaxed quasi-1D stereoregular polymeric chain, possibly with functional groups attached to each end, is (in the large- $N_c$  limit) equal to  $p_0$  plus an integer times the longitudinal period  $a$ . The quantity  $p_0$  is uniquely determined by the central region and is independent of the nature of the chain ends. As a consequence,  $p_0$  can be computed just by considering an infinite periodic chain, as in Eq. (16).

An equivalent statement concerns the end charges  $Q_{\text{end}}$  of the most general system and has been anticipated in Sec. II: they are quantized in the form  $Q_{\text{end}} = p_0/a$  plus an integer. Indeed, this statement has been heuristically confirmed using simple binary chains as test cases in Sec. II. The nonquantized term in the charge can be written, from Eq. (16),

$$\frac{p_0}{a} = \frac{1}{a} \sum_s Z_s z_s - \frac{1}{2\pi} \sum_{\sigma} \sum_{n=1}^{N_{\sigma}} \gamma_{\sigma n}. \quad (17)$$

We recall that in Eq. (17), we implicitly assume that both the nuclear coordinates  $z_s$  and the Wannier centers lie in the unit cell, the latter requirement being equivalent to fixing the  $2\pi$  arbitrariness in the Berry phases  $\gamma_{\sigma n}$ . If we relax this latter constraint, Eq. (17) automatically provides all the quantized values.

The case where the central region of the polymeric chain is centrosymmetric deserves a separate discussion. Assuming a *centrosymmetric origin* in Eq. (17) for such a system, we notice that the nuclear term is an integer multiple of  $1/2$ . As for the electronic term, centrosymmetry constrains the Berry phases  $\gamma_{\sigma n}$  to be equal to either  $0$  or  $\pi$  (*modulo*  $2\pi$ ). Hence, the electronic term contributes to  $p_0/a$  an integer multiple of  $1/2$  as well. When adding to this an arbitrary integer, the

final statement is that the end charges  $Q_{\text{end}}$  of the most general polymeric chain, whose bulk region is centrosymmetric, may only assume (in the large- $N_c$  limit) values which are integer multiples of  $1/2$ . We have previously anticipated this statement (Sec. II) and demonstrated it heuristically (Sec. III) using a simple binary chain as test case. Although we used for pedagogical purposes a strongly ionic system, the theorem is general and holds for systems of any ionicity. Furthermore, in all cases, the actual value of  $Q_{\text{end}}$  is determined, *within the set of quantized values*, by the chemical nature of the system.

### E. The correlated case

Throughout this work, we have worked at the level of single-particle approaches, such as HF or DFT. The specific tools used in our detailed proof (i.e., localized Boys'/Wannier orbitals) prevent us from directly extending the present proof to correlated wave function methods. Nonetheless, the exact quantization of end charges (in the large-system limit) still holds, as a robust topological phenomenon, even for correlated wavefunctions. In this respect, the phenomenon is similar to the fractional quantum Hall effect, where correlated wavefunctions are an essential ingredient.<sup>16</sup>

We have stated above that the bulk dipole per cell (or per monomer)  $p_0$  is defined in terms of Berry phases; more details about this can be found in our previous paper,<sup>26</sup> where a QC reformulation of the so-called “modern theory of polarization”<sup>7–10</sup> is presented. The ultimate reason for the occurrence of charge quantization is the *modulo*  $2\pi$  arbitrariness of any phase, as, e.g., in Eq. (17). A correlated wave function version of the modern theory of polarization, also based on Berry phases, does exist.<sup>10,27,28</sup> The quantization features, as discussed here for polymeric chains, remain unchanged. While not presenting a complete account here, we provide below the expression for  $p_0$  in the correlated case.

Suppose we loop the polymer onto itself along the  $z$  coordinate, with the loop of length  $L$ , where  $L$  equals  $a$  times the number of monomers. Let  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  be the many-body ground state wave function, where spin variables are omitted for the sake of simplicity. Since  $z$  is the coordinate along the loop,  $\Psi$  is periodic with period  $L$  with respect to the  $z_i$  coordinate of each electron. We define the (unitary and periodic) many-body operator

$$\hat{U} = e^{i(2\pi/L)\sum_{i=1}^N z_i}, \quad (18)$$

nowadays called the “twist” operator,<sup>28</sup> and the dimensionless quantity

$$\gamma = \text{Im} \ln \langle \Psi | \hat{U} | \Psi \rangle. \quad (19)$$

This  $\gamma$ , defined *modulo*  $2\pi$ , is a Berry phase in disguise, which is customarily called a “single-point” Berry phase.<sup>27</sup> In order to get  $p_0$  in the correlated case, it is enough to replace the sum of single-band Berry phases occurring in Eq. (17) with the many-body Berry phase  $\gamma$ , as defined in Eq. (19).

Notice that the large- $L$  limit of Eq. (19) is quite non-trivial, since as  $L$  increases,  $\hat{U}$  approaches the identity, but the number of electrons  $N$  in the wave function  $\Psi$  increases;

nonetheless, this limit *is* well-defined in insulators (and only in insulators).<sup>29,30</sup> In the special case where  $\Psi$  is a Slater determinant (i.e., uncorrelated single-particle approaches), the large- $L$  limit of  $\gamma$  converges to the sum of the Berry phases of the occupied bands, each given by Eq. (13). This result is proved in Refs. 10 and 27. Therefore, for a single-determinant  $\Psi$ , the correlated  $p_0$  defined via  $\gamma$  in Eq. (19) coincides (in the large- $L$  limit) with  $p_0$  discussed throughout this paper.

### V. CALCULATIONS FOR A CASE OF CHEMICAL INTEREST

Our realistic example is a set of fully conjugated *trans*-polyacetylene oligomers with the  $\text{C}_2\text{H}_2$  repeat unit ( $a = 4.670\,114\,817\,4$  a.u.), such as shown in Fig. 1. For the monomer unit, the bond distances and angles are  $r(\text{C}=\text{C}) = 1.363\text{\AA}$ ,  $r(\text{C}-\text{C}) = 1.428\text{\AA}$ ,  $r(\text{C}-\text{H}) = 1.09\text{\AA}$ ,  $\alpha(\text{CCC}) = 124.6^\circ$ , and  $\alpha(\text{C}=\text{C}-\text{H}) = 117.0^\circ$ . Note that due to alternating single-double carbon bond length, such a system is insulating. The chain with the equal carbon bonds would be conducting and, therefore, the theorem would not be applicable. The calculations were carried out at the RHF/30-21G level of the theory with the GAUSSIAN 03 code,<sup>6</sup> up to  $N_c = 257$   $\text{C}_2\text{H}_2$  units in the largest oligomer (Fig. 4). In order to save computational time, all the monomers were taken to be identical, i.e., each one with the same geometry. For the structure with the noncharged groups [Fig. 1(a)], we compute  $p(257) = 8.0 \times 10^{-7}$ , i.e., both  $p$ , and  $Q_{\text{end}}$  vanish, with a very small finite-size error. The charge-transfer structure [Fig. 1(b)] yields instead  $p(257) = 4.669\,728\,2$ , which corresponds to  $Q_{\text{end}} = 1$  to an accuracy of  $8.0 \times 10^{-5}$ . Thus, by modifying the end groups, one can observe the quantization theorem in a conjugated system, and again, the quantization is extremely accurate. For comparison, we have also carried out full periodic calculations<sup>31</sup> of the dipole moment via the Berry-phase approach,<sup>26,32</sup> utilizing 1024  $k$  points in the reciprocal space. Since these calculations were closed shell, the electronic dipole was computed for only one spin and then doubled. If the

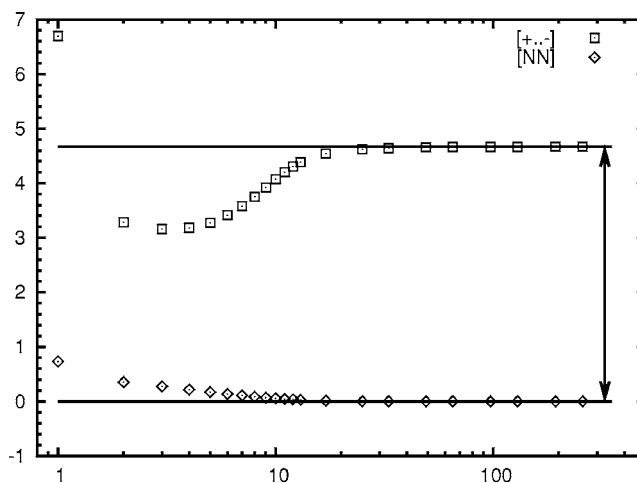


FIG. 4. Longitudinal dipole moment per monomer  $p(N_c)$  of the *trans*-polyacetylene oligomers, exemplified in Fig. 1, as a function of  $N_c$ : diamonds for the neutral structure [NN] [Fig. 1(a)] and squares for the charge-transfer structure [+...-] [Fig. 1(b)]. The double arrow indicates their difference, which is exactly equal to one quantum.

$C_2H_2$  unit cell is defined such that the cell boundaries cross the double bond, we get the periodic dipole value of exactly 0. On the other hand, with the cell boundaries bisecting the single bond, the dipole value is exactly 1 quantum or 4.670 114 817 4 a.u. (with half of this value per spin). Thus, in the periodic case, the quantum jump in the dipole can simply be obtained by changing the definition of the unit cell.

## VI. CONCLUSIONS

In conclusion, we have formulated and proved a theorem for the quantization of the dipole and the end charges in long polymeric chains. This is the analog of a well-known theorem in surface physics<sup>13</sup> but is proved here following a very different strategy and using the standard language of the QC literature on polymers.

An abridged statement of the present quantization theorem is that, for a quasi-1D stereoregular chain, the end charges are determined, *modulo an integer*, solely by a property of the bulk of the chain. This means that by changing the chain terminations, e.g., by attaching arbitrary functional groups at the chain ends, the end charges may only change by an integer (in the long-chain limit); correspondingly, the dipole may only change by an integer times  $a$  (lattice constant). The quantization rules have a topological character and are, therefore, extremely robust;<sup>16</sup> however, they become exact only asymptotically, in the large-system limit.

Due to the “bulk” origin, the allowed quantized dipole values can then be evaluated for the infinite chain, typically using the Berry-phase approach.<sup>26</sup> In the special case where the bulk of the chain is centrosymmetric, no computation is needed at all: the end charges may only be an integer multiple of  $1/2$ , as actually demonstrated above for the studied test cases.

The proof of the quantization theorem was carried out within the single-particle approach in the following steps: by mapping the finite and infinite quantum systems onto an equivalent system of point charges, by relating such finite and infinite systems to each other, and then by considering the most general finite system with arbitrary end groups. We believe that presenting the proof in this way, rather than following, for example, Ref. 13, illustrates the physical content of the theorem with greater detail. The case of a correlated wave function method is also mentioned, and while the quantization still holds, we do not prove it fully and only outline the steps necessary to reach such a conclusion.

The actual effects of this quantization were studied in a toy LiF chain and functionalized oligomers of polyacetylene. In both cases, the asymptotic quantization is readily approached, with deviations of the order of  $1.0 \times 10^{-4}$  for the largest oligomers considered. One of the effects worth noting in the polyacetylene oligomers is that the dipole per monomer is uniquely determined only *modulo* the unit length  $a$ , i.e., the same identical unit cell (i.e., bulk) gives rise to numerically different dipole values. Such a *modulo a* arbitrariness always arises within the periodic Berry-phase approach as, for example, demonstrated in Ref. 26. However, while in the periodic case, such an arbitrariness may appear to be just

a computational artifact of the Berry phases; here, we clearly see that, in fact, it corresponds to an actual physical effect that is observable in oligomer calculations. In general, the finite oligomer “chooses” one of the allowed quantized values, mandated by its bulk: which one? As we discussed, this depends on the chemical nature of the chain-end groups.

Finally, by utilizing the localization argument, one could readily predict the dipole moments of relevant push-pull systems where the charge transfer takes place. There, one only has to identify the groups between which the charge transfer occurs, and the actual end charges become readily available by utilizing the sequence of steps discussed in this paper.

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## APPENDIX: A WAY OF VISUALIZING THE END CHARGES

The net charges  $Q_{\text{end}}$  at the end of a long polymeric chain have been defined by means of a neutral rod having the same dipole  $d$  as the real system. There is an alternative pictorial way to visualize how and where there is charge accumulation on a long, though finite, polymeric chain. The appropriate tool is rather popular within the theory of semiconductor interfaces, where it has been given the name of “macroscopic average.”<sup>33</sup> In the present context, we are going to call the analogous tool a “sliding-window convolution.”

The total charge density of our finite system is

$$\rho(\mathbf{r}) = \sum_s Z_s \delta(\mathbf{r} - \mathbf{r}_s) + \rho_{\text{el}}(\mathbf{r}), \quad (\text{A1})$$

where  $\rho_{\text{el}}$  is the electronic-charge density. We define the 1D function  $\bar{\rho}(z)$  as the  $xy$  integral of  $\rho(\mathbf{r})$ ,

$$\begin{aligned} \bar{\rho}(z) &= \sum_s Z_s \delta(z - z_s) + \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \rho_{\text{el}}(\mathbf{r}) \\ &= \sum_s Z_s \delta(z - z_s) + \bar{\rho}_{\text{el}}(z). \end{aligned} \quad (\text{A2})$$

Since we are addressing stereoregular quasi-1D chains, in their bulk region, the function  $\bar{\rho}(z)$  is periodic with period  $a$  and deviates from periodicity in the end regions only. Clearly, for long chains (i.e., for large enough  $N_c$ ), the size of the end regions may depend on the chemical nature of the system but is *independent* of the actual value of  $N_c$ .

Besides being periodic, the function  $\bar{\rho}(z)$  averages to zero over one period  $a$ . We exploit this fact by defining the sliding-window convolution  $\bar{\bar{\rho}}(z)$  as

$$\begin{aligned}\bar{\rho}(z) &= \frac{1}{a} \int_{-a/2}^{a/2} dz' \bar{\rho}(z - z') \\ &= \frac{1}{a} \int_{-\infty}^{\infty} dz' \Theta(a/2 - |z - z'|) \bar{\rho}(z'),\end{aligned}\quad (\text{A3})$$

where  $\Theta$  is the Heaviside step function. In essence, the window convolution filters out the irrelevant periodic density oscillations and blows up in the regions where net charge accumulation occurs. By construction,  $\bar{\rho}(z)$  vanishes in the bulk region of the chain and, therefore, it visualizes the spatial extent of the “perturbation” due to the chain termination. By using Eq. (A2) into Eq. (A3) we have

$$\bar{\rho}(z) = \sum_s \frac{Z_s}{a} \Theta(a/2 - |z - z_s|) + \frac{1}{a} \int_{-a/2}^{a/2} dz' \bar{\rho}_{\text{el}}(z - z'), \quad (\text{A4})$$

which also explicitly shows how the filter broadens the  $\delta$ -like nuclear charge density, resulting in a kind of histogram.

<sup>1</sup> ABINIT see <http://www.abinit.org/>

<sup>2</sup> CRYSTAL 06 see <http://www.crystal.unito.it/>

<sup>3</sup> SIESTA see <http://www.uam.es/departamentos/ciencias/fismateriac/siesta/>

<sup>4</sup> VASP see <http://cms.mpi.univie.ac.at/vasp/>

<sup>5</sup> Quantum EXPRESSO see <http://www.pwscf.org>

<sup>6</sup> GAUSSIAN 03, revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K.

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