Correct Description of the Bond Dissociation Limit without Breaking Spin Symmetry by a Random-Phase-Approximation Correlation Functional

Andreas Heßelmann and Andreas Görling

Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany

(Received 24 September 2010; published 28 February 2011)

A correlation functional that is termed exact-exchange random phase approximation (EXX-RPA) functional and is obtained with the exact frequency-dependent exchange kernel via the fluctuation-dissipation theorem is shown to correctly describe electron pair bonds in the dissociation limit without the need to resort to symmetry breaking in spin space. Because the functional also yields more accurate electronic energies for molecules in their equilibrium geometry than standard correlation functionals, it combines accuracy at equilibrium bond distances and in dissociation processes with a correct description of spin, something all commonly employed correlation functionals fail to do. The reason why the EXX-RPA correlation functional yields distinctively and qualitatively better results than RPA approaches based on Hartree-Fock and time-dependent Hartree-Fock is explained.

DOI: 10.1103/PhysRevLett.106.093001 PACS numbers: 31.15.ae, 31.10.+z, 31.15.V−

Despite their ubiquitous application, present density-functional methods or more precisely Kohn-Sham (KS) methods, i.e., methods based on density functionals in the generalized gradient approximation or hybrid methods like the B3LYP method, suffer from severe shortcomings. The most serious problem of present KS methods, besides their inability to treat van der Waals interactions, is that they cannot correctly treat bond dissociation in molecules. The prototype dissociation of a chemical bond is the dissociation of the H_2 molecule. Standard nonspin-polarized KS calculations, as well as nonspin-polarized Hartree-Fock calculations, do yield qualitatively wrong electronic energies for larger bond distances and, in the limit of infinite distances, do not yield an electronic energy equal to twice the energy of an isolated hydrogen atom. By resorting to spin-polarized calculations, a qualitatively correct electronic energy is obtained at large distances which leads to a qualitatively correct potential energy curve, however, at the price of a qualitatively wrong spin-density. From a certain bond length on, termed the Coulson-Fisher point, alpha and beta electron densities in a spin-polarized calculation no longer are equal as they should be for an electronic state which, at all bond distances, is a singulet.

The problem occurs generally when dissociating electron pair bonds. Therefore, a lot of work has been attributed to it [1–8], with the goal to devise a KS approach that is generally applicable, performs well at equilibrium bond distances, and at the same time describes qualitatively correct bond breaking. We here show that a recent correlation functional [9] obtained within the framework of the random phase approximation (RPA) with the frequency-dependent exact-exchange (EXX) kernel [10] of time-dependent density-functional theory (TDDFT) leads to a correct dissociation of the H_2 molecule as well as other molecules.

RPA correlation functionals have attracted considerable interest in recent years [3,4,9,11–18]. The EXX-RPA correlation functional considered here is unique because it not only describes the dissociation limit correctly but also leads to electronic energies of molecules at equilibrium distances and to reaction energies that are more accurate than those from standard generalized gradient approximation or hybrid DFT methods [9] and because it enables a description of van der Waals interactions. Moreover, the basic EXX-RPA correlation functional can easily be modified and further developed; see below. Therefore, this EXX-RPA functional seems to be a highly promising starting point for a new family of functionals.

As usual in KS methods, an EXX-RPA calculation consists of two steps. (i) The KS orbitals and eigenvalues are calculated. This is done by an EXX-KS calculation [19] which means treating exactly the local multiplicative KS exchange potential, which must not be confused with the nonlocal HF exchange potential, but neglects the correlation potential. (ii) The electronic energy is calculated. It is the sum of the EXX energy plus the correlation energy from the EXX-RPA correlation functional obtained with the EXX kernel. One can easily imagine modifications of this approach by including a correlation potential in step (i) or a correlation contribution to the EXX kernel in step (ii). Here we concentrate on the basic EXX-RPA correlation functional.

An important, however, unexplained finding in Ref. [9] is that for the molecules considered in that work (molecules in their equilibrium geometry) the results from the EXX-RPA approach are distinctively better than those from an RPA method based on HF and time-dependent HF (TDHF), which shall be denoted as HF-RPA here. The EXX-KS and the HF determinants and thus the EXX and the HF electronic energies are known to be very close to each other [20]. Moreover, the excitation energies from a

TDDFT calculation with the EXX kernel, i.e., a TDEXX calculation, and a TDHF calculation are known to be very similar [21,22]. Therefore, one might also assume that the RPA correlation energies and the resulting complete electronic energies are close. This, however, was found in Ref. [9] not to be the case. Here we make the same finding in the case of H_2 dissociation [see Fig. 1], which is even more striking. Because H_2 is a two-electron system, the occupied EXX and HF orbital and thus the EXX and HF electronic energies are exactly identical. Moreover the TDEXX and the TDHF excitations energies are exactly identical. Nevertheless, the HF-RPA approach leads to a potential energy curve of H_2 that differs strongly from the exact one while the EXX-RPA approach yields a potential energy curve approaching the correct dissociation energy at a bond distance of about 20 a.u. This is shown in Fig. 1 which displays EXX and HF potential energy curves, which are identical, and potential energy curves with the EXX-RPA and HF-RPA correlation energy included, which are distinctively different. Note that the orbitals that enter the EXX-RPA functional are the EXX orbitals from a restricted Kohn-Sham calculation and not, as in Ref. [4], orbitals that are recalculated from electron densities of spin-polarized calculations, which approach the exact electron density for large bond distances. A second central result of this work is the explanation why EXX-RPA and HF-RPA results are different.

For a two-electron case like H_2 the KS exchange potential is just half of the negative of the Coulomb potential. Therefore, an EXX calculation for a two-electron system can easily be carried out without the necessity to invoke optimized effective potential methods [19,23] as it is usually required for EXX calculations. Similarly, for a two-electron system, the sum of the Coulomb and exchange kernel equals just half the Coulomb kernel and is therefore frequency-independent. Calculations in this work were carried out with the program package MOLPRO [24]. For H_2 the aug-cc-pVQZ basis set of Ref. [25] was used.

The basis of the RPA correlation functional in density-functional theory is the fluctuation-dissipation theorem [11]. It enables us to express the KS correlation energy according to

$$E_c = \frac{-1}{2\pi}\int_0^1 d\alpha \int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty d\omega[\chi_\alpha(\mathbf{r},\mathbf{r}',i\omega) - \chi_0(\mathbf{r},\mathbf{r}',i\omega)]. \quad (1)$$

The central quantity required in expression (1) for the correlation energy is the frequency- and coupling-strength-dependent response function χ_α. For a coupling constant of $\alpha = 0$, χ_α is the KS response function which is known in terms of the KS orbitals and eigenvalues. For all other values of the coupling strength α the response function χ_α, or its frequency integral, is calculated by TDDFT. For the EXX-RPA correlation energy the coupling-strength-dependent TDEXX equation

$$[\boldsymbol{\varepsilon}^2 + \alpha\boldsymbol{\varepsilon}^{1/2}(\mathbf{A}+\mathbf{B}+\boldsymbol{\Delta})\boldsymbol{\varepsilon}^{1/2}]\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)[\mathbf{1} - \alpha\boldsymbol{\varepsilon}^{-1/2}(\mathbf{A}-\mathbf{B}+\boldsymbol{\Delta})\boldsymbol{\varepsilon}^{-1/2}]\mathbf{z}_n(\alpha). \quad (2)$$

is solved. Equation (2) is obtained from the TDEXX equation derived in Refs. [21,22] for the full coupling strength $\alpha = 1$ by simply multiplying all terms originating from the sum of the Coulomb and exchange kernel by the coupling strength α exploiting the fact that these kernels are linear in α. The matrices $\mathbf{A}$, $\mathbf{B}$, $\boldsymbol{\Delta}$, and $\boldsymbol{\varepsilon}$ with a dimension equal to the number of occupied times unoccupied KS orbitals contain the matrix elements $A_{ia,jb} = 2(ai|jb) - (ab|ji)$, $B_{ia,jb} = 2(ai|bj) - (aj|bi)$, $\Delta_{ia,jb} = \delta_{ij}\langle\varphi_a|\hat{v}_x^{\mathrm{NL}} - \hat{v}_x|\varphi_b\rangle - \delta_{ab}\langle\varphi_i|\hat{v}_x^{\mathrm{NL}} - \hat{v}_x|\varphi_j\rangle$, and $\varepsilon_{ia,jb} = \delta_{ia,jb}(\varepsilon_i - \varepsilon_a)$ with φ_i and φ_j being occupied KS orbitals with eigenvalues ε_i and ε_j, φ_a and φ_b being unoccupied KS orbitals with eigenvalues ε_a and ε_b, and with integrals of the type $(ai|jb)$ being defined according to $\int d\mathbf{r}d\mathbf{r}'\varphi_a(\mathbf{r})\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_b(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. The indices ia and jb are superindices labeling the columns and rows of the matrices. The operator $\hat{v}_x^{\mathrm{NL}}$ is a nonlocal exchange operator of the form of the HF exchange operator but is constructed from KS orbitals, while $\hat{v}_x$ is the operator corresponding to the local multiplicative KS exchange potential. The eigenvectors $\mathbf{z}_n(\alpha)$ and the eigenfrequencies $\Omega_n(\alpha)$ of the TDEXX equation [9] then yield the EXX-RPA correlation energy according to

$$E_c = \int_0^1 d\alpha V_c(\alpha) \quad (3)$$

with the sum-over-excitations integrand

$$V_c(\alpha) = \left[\sum_n \mathbf{z}_n^T(\alpha)\boldsymbol{\varepsilon}^{1/2}\mathbf{C}\boldsymbol{\varepsilon}^{1/2}\mathbf{z}_n(\alpha)/\Omega_n(\alpha)\right] - \mathrm{Tr}[\mathbf{C}] \quad (4)$$

with the matrix $\mathbf{C}$ containing the matrix elements $C_{ia,jb} = (ai|jb)$. The coupling strength integration in Eq. (3) is carried out numerically.

For the HF-RPA correlation energy instead of the TDEXX Eq. (2) the TDHF equation is solved. The latter can be written in the form [20,22]

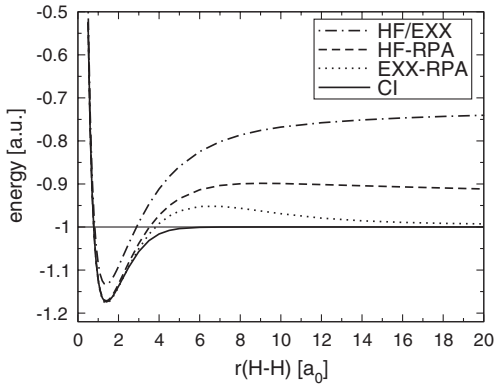

FIG. 1. Potential energy curves of the H_2 molecule.

$$[\boldsymbol{\varepsilon}^2 + \alpha\boldsymbol{\varepsilon}_{\mathrm{HF}}^{1/2}(\mathbf{A}_{\mathrm{HF}} + \mathbf{B}_{\mathrm{HF}})\boldsymbol{\varepsilon}_{\mathrm{HF}}^{1/2}]\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)[\mathbf{1} + \alpha\boldsymbol{\varepsilon}_{\mathrm{HF}}^{-1/2}(\mathbf{A}_{\mathrm{HF}} - \mathbf{B}_{\mathrm{HF}})\boldsymbol{\varepsilon}_{\mathrm{HF}}^{-1/2}]^{-1}\mathbf{z}_n(\alpha). \quad (5)$$

The matrices $\mathbf{A}_{\mathrm{HF}}$, $\mathbf{B}_{\mathrm{HF}}$, and $\varepsilon_{\mathrm{HF}}$ now are defined with respect to HF instead of EXX orbitals, indicated by the subscript HF. If the resulting excitation energies $\Omega_n(\alpha)$ and eigenvectors $\mathbf{z}_n(\alpha)$ are inserted into Eqs. (4) and (3) then the HF-RPA correlation energy results.

If the differences between HF and EXX determinants that are known to be very small [20] are neglected, then the occupied as well as the unoccupied EXX and HF orbitals are related by a unitary transformation. It is then possible to express the TDHF Eq. (5) in terms of EXX orbitals; for details see Refs. [20,22],

$$\{\boldsymbol{\varepsilon}^2 + \boldsymbol{\varepsilon}^{1/2}[\alpha(\mathbf{A} + \mathbf{B}) + \boldsymbol{\Delta}]\boldsymbol{\varepsilon}^{1/2}\}\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)\{\mathbf{1} + \boldsymbol{\varepsilon}^{-1/2}[\alpha(\mathbf{A} - \mathbf{B}) + \boldsymbol{\Delta}]\boldsymbol{\varepsilon}^{-1/2}\}^{-1}\mathbf{z}_n(\alpha). \quad (6)$$

The matrix $\boldsymbol{\Delta}$ arises from the transformation of the diagonal matrix $\boldsymbol{\varepsilon}$HF containing the differences of HF eigenvalues into the sum $\boldsymbol{\varepsilon} + \boldsymbol{\Delta}$ referring to EXX eigenvalue differences and EXX orbitals. Therefore the matrix $\boldsymbol{\Delta}$ is not scaled by the coupling constant α in the TDHF Eq. (6) in contrast to the TDEXX Eq. (2).

In case of two electron systems, the matrix $\boldsymbol{\Delta}$ contains only elements $\Delta_{ia,ib}$ because there is only one occupied orbital, φ_i, and these matrix elements are given by $\Delta_{ia,ib} = -(ai|ib) + (ab|ii)$ because the nonlocal exchange potential $\hat{v}_x^{\mathrm{NL}}$ is constructed exclusively from the one occupied orbital φ_i and the KS exchange potential is just the negative of the Coulomb potential of the electron density of the orbital φ_i. As a result, the terms in the TDEXX Eq. (2) simplify according to $[\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] = 2\mathbf{C}$ and $[\mathbf{A} - \mathbf{B} + \boldsymbol{\Delta}] = \mathbf{0}$ and the equation assumes the form

$$[\boldsymbol{\varepsilon}^2 + 2\alpha\boldsymbol{\varepsilon}^{1/2}\mathbf{C}\boldsymbol{\varepsilon}^{1/2}]\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)\mathbf{z}_n(\alpha). \quad (7)$$

The TDEXX Eq. (7) for two-electron systems contains a kernel equal to half the Coulomb kernel. (A direct RPA equation would contain the full Coulomb kernel.)

Similarly, also Eq. (6), the TDHF equation expressed in EXX orbitals, simplifies for two-electron systems to

$$[\boldsymbol{\varepsilon}^2 + 2\alpha\boldsymbol{\varepsilon}^{1/2}\mathbf{C}\boldsymbol{\varepsilon}^{1/2} + (1 - \alpha)\boldsymbol{\varepsilon}^{1/2}\boldsymbol{\Delta}\boldsymbol{\varepsilon}^{1/2}]\mathbf{z}_n(\alpha) = \Omega_n^2(\alpha)[\mathbf{1} + (1 - \alpha)\boldsymbol{\varepsilon}^{-1/2}\boldsymbol{\Delta}\boldsymbol{\varepsilon}^{-1/2}]^{-1}\mathbf{z}_n(\alpha). \quad (8)$$

For two-electron systems the HF and the EXX determinants are exactly equal. Therefore, Eq. (8) is the exact TDHF equation for two-electron systems just expressed in KS orbitals. The crucial point is that the TDEXX Eq. (7) and the TDHF Eq. (8) are equal only for a coupling strength of $\alpha = 1$. This means for all $\alpha \neq 1$ the TDHF and TDEXX excitation energies $\Omega_n(\alpha)$ of two-electron systems and the corresponding eigenvectors $\mathbf{z}_n(\alpha)$ differ. As a consequence the electron-electron contribution $V_c(\alpha)$ in Eq. (4) differs for $\alpha \neq 1$ and $\alpha \neq 0$. [For $\alpha = 0$ $V_c(\alpha)$ in any case equals zero.]

In Fig. 2 $V_c(\alpha)$ is displayed for EXX-RPA and HF-RPA for different H_2 bond distances. Figure 2 shows that the differences in $V_c(\alpha)$ are significant. Such strong differences in the α dependence of $V_c(\alpha)$ not only occur for H_2 but are present in general; see, e.g., $V_c(\alpha)$ curves for the water molecule in the supporting information. The differences between the TDEXX Eqs. (2) and (7) and the TDHF equation expressed in EXX orbitals, Eqs. (6) and (8), that are responsible for most (all, in the H_2 case) of the differences between EXX-RPA and HF-RPA arise from the fact that the matrix $\boldsymbol{\Delta}$ resulting from the transformation of HF to EXX eigenvalue differences is not scaled by the coupling constant in the HF-RPA case. This leads to terms $(1 - \alpha)\Delta$ in the TDHF equations not present in the TDEXX equations.

The differences between HF-RPA and EXX-RPA can also be rationalized as follows. The RPA correlation energy according to Eq. (1) depends on the response function χ_α at all values $0 \leq \alpha \leq 1$. At $\alpha = 1$ TDHF and TDEXX excitation energies Ω_n and the associated eigenvalues $\mathbf{z}_n$ are quite similar (identical for H_2) and, therefore, the corresponding response functions $\chi_{\alpha=1}$ are quite similar. However, at $\alpha = 0$ the response function is given by a sum-over-states expression containing occupied and unoccupied orbitals and differences of the orbital eigenvalues. The unoccupied HF and EXX orbitals and their

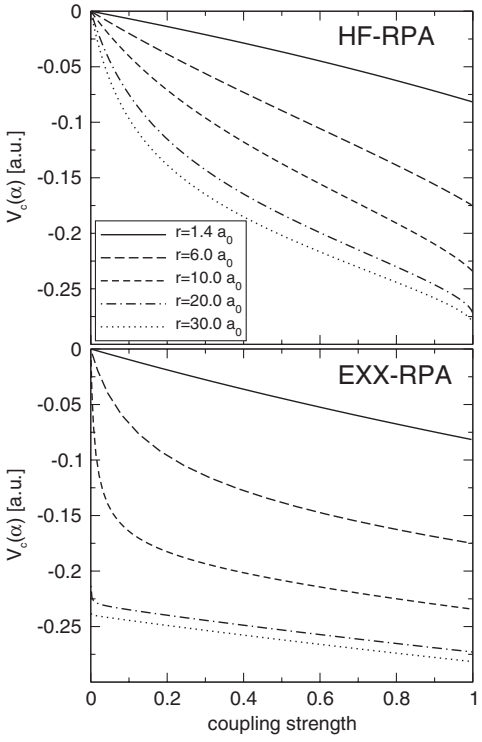

FIG. 2. Coupling strength integrand [Eq. (4)] for HF-RPA (top panel) and EXX-RPA (bottom panel) plotted for several H-H bond distances.

eigenvalues differ strongly and as a result the response function χ_α is also strongly different at $\alpha = 0$. Indeed, in most cases, unoccupied HF orbitals have positive eigenvalues and individually have little physical meaning in contrast to EXX orbitals and their eigenvalues. Because the response function changes continuously along the adiabatic connection, i.e., along α, the response functions are strongly different for all values of α that are not close to 1. The resulting better performance of EXX-RPA compared to HF-EXX correlation functionals, in this sense, to some extent is a consequence of the physically more meaningful EXX orbital and eigenvalue spectrum.

Figure 2 shows that for increasing H_2 bond distance the electron-electron contribution V_c to the correlation energy as a function $V_c(\alpha)$ of the coupling constant α jumps immediately next to $\alpha = 0$ from zero to a lower energy that equals the static correlation energy given by the integral $-(ia|ia)$ with i referring to the occupied and a referring to the lowest unoccupied orbital. This static correlation contribution exclusively arises from the contribution of the energetically lowest excitation (excitation from bonding to the antibonding linear combination of 1s orbitals) to the total EXX-RPA correlation energy of Eqs. (4) and (3); see supplementary material for details [26]. The jump of V_c is in agreement with the finding of Ref. [8] where the exact $V_c(\alpha)$ was determined for small systems using a full configuration interaction method. The exact curve for $V_c(\alpha)$ of Ref. [8] jumps to a horizontal line which shows that the static correlation energy is independent of the coupling constant. The fact that the EXX-RPA $V_c(\alpha)$ curve after the jump shows a slight slope can be attributed to dynamic correlation which arises from the contributions of other excitations to the correlation energy. This dynamic correlation corrects contributions to the EXX energy arising because the EXX orbitals are not linear combinations of the exact atomic hydrogen 1s orbitals (see supplementary material for details [26]).

For H_2 bond distances around 6 a.u., a hump occurs in the EXX-RPA potential energy curve; see Fig. 1. The reason is that for this distance $V_c(\alpha)$ does not yet jump to the full static correlation energy [see Fig. 2] and, therefore, the EXX-RPA correlation functional does not yet yield the full static correlation energy $-(ia|ia)$ of -0.178 a.u. but only -0.108 a.u., which is the contribution from the energetically lowest excitation energy to $V_c(\alpha)$; see supplementary material for details [26].

The EXX-RPA method not only describes the dissociation limit of H_2 correctly, but of molecular bonds in general. Results for molecules like N_2, CO, or HF will be presented elsewhere. The EXX-RPA functional, therefore, is a general purpose functional that seems to be superior to commonly employed correlation functionals.

We acknowledge funding by the German Research Council (DFG) through the Cluster of Excellence "Engineering of Advanced Materials" at the University of Erlangen-Nuremberg.

[1] O. V. Gritsenko and E. J. Baerends, Phys. Rev. A **54**, 1957 (1996).
[2] E. J. Baerends, Phys. Rev. Lett. **87**, 133004 (2001).
[3] F. Furche, Phys. Rev. B**64**, 195120 (2001).
[4] M. Fuchs, Y. M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. **122**, 094116 (2005).
[5] M. J. G. Peach, A. M. Teale, and D. J. Tozer, J. Chem. Phys. **126**, 244104 (2007).
[6] D. G. Tempel, T. J. Martinez, and N. T. Maitra, J. Chem. Theory Comput. **5**, 770 (2009).
[7] N. Helbig, I. V. Tokatly, and A. Rubio, J. Chem. Phys. **131**, 224105 (2009).
[8] A. M. Teale, S. Coriani, and T. Helgaker, J. Chem. Phys. **132**, 164115 (2010).
[9] A. Heßelmann and A. Görling, Mol. Phys. **108**, 359 (2010).
[10] A. Görling, Int. J. Quantum Chem. **69**, 265 (1998).
[11] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).
[12] J. F. Dobson and J. Wang, Phys. Rev. Lett. **82**, 2123 (1999).
[13] F. Furche, J. Chem. Phys. **129**, 114105 (2008).
[14] H. Jiang and E. Engel, J. Chem. Phys. **127**, 184108 (2007).
[15] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **131**, 034110 (2009).
[16] J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Angyan, Phys. Rev. Lett. **102**, 096404 (2009).
[17] A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Chem. Theory Comput. **6**, 127 (2010).
[18] M. Hellgren and U. v. Barth, J. Chem. Phys. **132**, 044101 (2010).
[19] A. Heßelmann, A. W. Götz, F. Della Sala, and A. Görling, J. Chem. Phys. **127**, 054102 (2007).
[20] A. Ipatov, A. Heßelmann, and A. Görling, Int. J. Quantum Chem. **110**, 2202 (2010).
[21] A. Heßelmann, A. Ipatov, and A. Görling, Phys. Rev. A **80**, 012507 (2009).
[22] A. Heßelmann and A. Görling, J. Chem. Phys., **134**, 034120 (2011).
[23] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[24] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz *et al.*, (2010), http://www.molpro.net.
[25] J. T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[26] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.106.093001.