Your article (QUA-2004-0093) from International Journal of Quantum Chemistry is available for download
=====
International Journal of Quantum Chemistry Published by John Wiley & Sons, Inc.

Dear Author,

Your page proofs are available in PDF format; please refer to this URL address
http://rapidproof.cadmus.com/RapidProof/retrieval/index.jsp

Login: your e-mail address
Password: ----

The site contains 1 file. You will need to have Adobe Acrobat Reader software to read these files. This is free software and is available for user downloading at http://www.adobe.com/products/acrobat/readstep.html. If you have the Notes annotation tool (not contained within Acrobat reader), you can make corrections electronically and return them to Wiley as an e-mail attachment (see the Notes tool instruction sheet). Alternatively, if you would prefer to receive a paper proof by regular mail, please contact Melissa Lutchkus(e-mail: lutchkusm@cadmus.com, phone: 800-238-3814 (X 662)or 717-721-2662). Be sure to include your article number.

This file contains:

Author Instructions Checklist
Adobe Acrobat Users - NOTES tool sheet
Reprint Order form
Copyright Transfer Agreement
Return fax form
A copy of your page proofs for your article

After printing the PDF file, please read the page proofs carefully and:

1) indicate changes or corrections in the margin of the page proofs;
2) answer all queries (footnotes A,B,C, etc.) on the last page of the PDF proof;
3) proofread any tables and equations carefully;
4) check that any Greek, especially "mu", has translated correctly.

Special Notes:

1. Figure(s) ___________ are unacceptable for publication. Please supply good quality hard copy (and/or TIFF or EPS files) when you return your page proofs.

Within 48 hours, please fax or e-mail the following to the address given below:

1) original PDF set of page proofs,
2) print quality hard copy figures for corrections and/or TIFF or EPS files of figures for correction (if necessary),
3) Signed Copyright Transfer Agreement,
4) Reprint Order form,
5) Return fax form

International Journal of Quantum Chemistry

Copy of e-mail Notification zqz1361

Return to:

Christine Haller, Production Editor
Cadmus Professional Communications
300 West Chestnut Street
Ephrata, PA 17522
U.S.A.
(See fax number and e-mail address below.)

If you experience technical problems, please contact Melissa Lutchkus (e-mail: lutchkusm@cadmus.com, phone: 800-238-3814 (X 662) or 717-721-2662). Be sure to include your article number.

If you have any questions regarding your article, please contact me. PLEASE ALWAYS INCLUDE YOUR ARTICLE NO. (QUA-2004-0093) WITH ALL CORRESPONDENCE.

This e-proof is to be used only for the purpose of returning corrections to the publisher.

Sincerely,

Christine Haller, Production Editor
E-mail: hallerc@cadmus.com
Tel: 800-238-3814 (X 627)
Fax: 717-738-9444

Publishers Since 1807

111 River Street, Hoboken, NJ 07030

*****IMMEDIATE RESPONSE REQUIRED*****

Please follow these instructions to avoid delay of publication.

☐ **READ PROOFS CAREFULLY**

- This will be your only chance to review these proofs.
- Please note that the volume and page numbers shown on the proofs are for position only.

☐ **ANSWER ALL QUERIES ON PROOFS** (Queries for you to answer are attached as the last page of your proof.)

- Mark all corrections directly on the proofs. Note that excessive author alterations may ultimately result in delay of publication and extra costs may be charged to you.

☐ **CHECK FIGURES AND TABLES CAREFULLY** (Color figures will be sent under separate cover.)

- Check size, numbering, and orientation of figures.
- All images in the PDF are downsampled (reduced to lower resolution and file size) to facilitate Internet delivery. These images will appear at higher resolution and sharpness in the printed article.
- Review figure legends to ensure that they are complete.
- Check all tables. Review layout, title, and footnotes.

☐ **COMPLETE REPRINT ORDER FORM**

- Fill out the attached reprint order form. It is important to return the form even if you are not ordering reprints. You may, if you wish, pay for the reprints with a credit card. Reprints will be mailed only after your article appears in print. This is the most opportune time to order reprints. If you wait until after your article comes off press, the reprints will be considerably more expensive.

RETURN
☐ **PROOFS**
☐ **REPRINT ORDER FORM**
☐ **CTA (If you have not already signed one)**

RETURN WITHIN 48 HOURS OF RECEIPT VIA FAX TO 1-717-738-9444

QUESTIONS?

Christine Haller, Production Editor
Phone: 800-238-3814 ext. 627
E-mail: hallerc@cadmus.com
Refer to journal acronym and article production number

Softproofing for advanced Adobe Acrobat Users - NOTES tool

NOTE: ACROBAT READER FROM THE INTERNET DOES NOT CONTAIN THE NOTES TOOL USED IN THIS PROCEDURE.

Acrobat annotation tools can be very useful for indicating changes to the PDF proof of your article. By using Acrobat annotation tools, a full digital pathway can be maintained for your page proofs.

The NOTES annotation tool can be used with either Adobe Acrobat 3.0x or Adobe Acrobat 4.0. Other annotation tools are also available in Acrobat 4.0, but this instruction sheet will concentrate on how to use the NOTES tool. Acrobat Reader, the free Internet download software from Adobe, DOES NOT contain the NOTES tool. In order to softproof using the NOTES tool you must have the full software suite Adobe Acrobat Exchange 3.0x or Adobe Acrobat 4.0 installed on your computer.

Steps for Softproofing using Adobe Acrobat NOTES tool:

1. Open the PDF page proof of your article using either Adobe Acrobat Exchange 3.0x or Adobe Acrobat 4.0. Proof your article on-screen or print a copy for markup of changes.

2. Go to File/Preferences/Annotations (in Acrobat 4.0) or File/Preferences/Notes (in Acrobat 3.0) and enter your name into the “default user” or “author” field. Also, set the font size at 9 or 10 point.

3. When you have decided on the corrections to your article, select the NOTES tool from the Acrobat toolbox and click in the margin next to the text to be changed.

4. Enter your corrections into the NOTES text box window. Be sure to clearly indicate where the correction is to be placed and what text it will effect. If necessary to avoid confusion, you can use your TEXT SELECTION tool to copy the text to be corrected and paste it into the NOTES text box window. At this point, you can type the corrections directly into the NOTES text box window. **DO NOT correct the text by typing directly on the PDF page.**

5. Go through your entire article using the NOTES tool as described in Step 4.

6. When you have completed the corrections to your article, go to File/Export/Annotations (in Acrobat 4.0) or File/Export/Notes (in Acrobat 3.0). Save your NOTES file to a place on your harddrive where you can easily locate it. **Name your NOTES file with the article number assigned to your article in the original softproofing e-mail message.**

7. **When closing your article PDF be sure NOT to save changes to original file.**

8. To make changes to a NOTES file you have exported, simply re-open the original PDF proof file, go to File/Import/Notes and import the NOTES file you saved. Make changes and re-export NOTES file keeping the same file name.

9. When complete, attach your NOTES file to a reply e-mail message. Be sure to include your name, the date, and the title of the journal your article will be printed in.

John Wiley & Sons, Inc.

Publishers Since 1807

REPRINT BILLING DEPARTMENT • 111 RIVER STREET • HOBOKEN, NJ 07030
PHONE: (201) 748-8789; FAX: (201) 748-6326
E-MAIL: reprints @ wiley.com

PREPUBLICATION REPRINT ORDER FORM

Please complete this form even if you are not ordering reprints. This form **MUST** be returned with your corrected proofs and original manuscript. Your reprints will be shipped approximately 4 weeks after publication. Reprints ordered after printing are substantially more expensive.

JOURNAL: *INT'L JOURNAL OF QUANTUM CHEMISTRY*_____ VOLUME_____ ISSUE_____

TITLE OF MANUSCRIPT____

MS. NO.____________ NO. OF PAGES______ AUTHOR(S)______________________________

**50 Reprints will be supplied free of charge

REPRINTS 8 1/4 X 11

No. of Pages	100 Reprints	200 Reprints	300 Reprints	400 Reprints	500 Reprints
	$	$	$	$	$
1-4	336	501	694	890	1,052
5-8	469	703	987	1,251	1,477
9-12	594	923	1,234	1,565	1,850
13-16	714	1,156	1,527	1,901	2,273
17-20	794	1,340	1,775	2,212	2,648
21-24	911	1,529	2,031	2,536	3,037
25-28	1,004	1,707	2,267	2,828	3,388
29-32	1,108	1,894	2,515	3,135	3,755
33-36	1,219	2,092	2,773	3,456	4,143
37-40	1,329	2,290	3,033	3,776	4,528

** REPRINTS ARE ONLY AVAILABLE IN LOTS OF 100. IF YOU WISH TO ORDER MORE THAN 500 REPRINTS, PLEASE CONTACT OUR REPRINTS DEPARTMENT AT (201)748-8789 FOR A PRICE QUOTE.

COVERS

100 Covers - $90 • 200 Covers - $145 • 300 Covers - $200
400 Covers - $255 • 500 Covers - $325 • Additional 100s - $65

❑ Please send me __________ reprints of the above article at....................... $____________
❑ Please send me __________ Generic covers of the above journal at...................... $____________
Please add appropriate State and Local Tax {Tax Exempt No.__________________} $____________
Please add 5% Postage and Handling.. $____________
TOTAL AMOUNT OF ORDER** .... $____________

***International orders must be paid in U.S. currency and drawn on a U.S. bank*

Please check one: ❑ Check enclosed ❑ Bill me ❑ Credit Card
If credit card order, charge to: ❑ American Express ❑ Visa ❑ MasterCard ❑ Discover
Credit Card No.____________________________ Signature___________________________ Exp. Date___________

Bill To:
Name____
Address/Institution_____________________________
____
____
____

Ship To:
Name____
Address/Institution_____________________________
____
____
____

Purchase Order No. ______________________________ Phone ________________ Fax ________________
E-mail: ___________________________________

111 River Street
Hoboken, NJ 07030
201.748.6000
FAX 201.748.6052

COPYRIGHT TRANSFER AGREEMENT

Date:

To:

Production/Contribution
ID# _______________
Publisher/Editorial office use only

Re: Manuscript entitled____
____(the "Contribution")
for publication in ____(the "Journal")
published by Wiley Periodicals, Inc. ("Wiley").

Dear Contributor(s):

Thank you for submitting your Contribution for publication. In order to expedite the editing and publishing process and enable Wiley to disseminate your work to the fullest extent, we need to have this Copyright Transfer Agreement signed and returned to us as soon as possible. If the Contribution is not accepted for publication this Agreement shall be null and void.

A. **COPYRIGHT**

1. The Contributor assigns to Wiley, during the full term of copyright and any extensions or renewals of that term, all copyright in and to the Contribution, including but not limited to the right to publish, republish, transmit, sell, distribute and otherwise use the Contribution and the material contained therein in electronic and print editions of the Journal and in derivative works throughout the world, in all languages and in all media of expression now known or later developed, and to license or permit others to do so.

2. Reproduction, posting, transmission or other distribution or use of the Contribution or any material contained therein, in any medium as permitted hereunder, requires a citation to the Journal and an appropriate credit to Wiley as Publisher, suitable in form and content as follows: (Title of Article, Author, Journal Title and Volume/Issue Copyright © [year] Wiley Periodicals, Inc. or copyright owner as specified in the Journal.)

B. **RETAINED RIGHTS**

Notwithstanding the above, the Contributor or, if applicable, the Contributor's Employer, retains all proprietary rights other than copyright, such as patent rights, in any process, procedure or article of manufacture described in the Contribution, and the right to make oral presentations of material from the Contribution.

C. **OTHER RIGHTS OF CONTRIBUTOR**

Wiley grants back to the Contributor the following:

1. The right to share with colleagues print or electronic "preprints" of the unpublished Contribution, in form and content as accepted by Wiley for publication in the Journal. Such preprints may be posted as electronic files on the Contributor's own website for personal or professional use, or on the Contributor's internal university or corporate networks/intranet, or secure external website at the Contributor's institution, but not for commercial sale or for any systematic external distribution by a third party (e.g., a listserve or database connected to a public access server). Prior to publication, the Contributor must include the following notice on the preprint: "This is a preprint of an article accepted for publication in [Journal title] © copyright (year) (copyright owner as specified in the Journal)". After publication of the Contribution by Wiley, the preprint notice should be amended to read as follows: "This is a preprint of an article published in [include the complete citation information for the final version of the Contribution as published in the print edition of the Journal]", and should provide an electronic link to the Journal's WWW site, located at the following Wiley URL: http://www.interscience.Wiley.com/. The Contributor agrees not to update the preprint or replace it with the published version of the Contribution.

2. The right, without charge, to photocopy or to transmit online or to download, print out and distribute to a colleague a copy of the published Contribution in whole or in part, for the colleague's personal or professional use, for the

advancement of scholarly or scientific research or study, or for corporate informational purposes in accordance with Paragraph D.2 below.

3. The right to republish, without charge, in print format, all or part of the material from the published Contribution in a book written or edited by the Contributor.

4. The right to use selected figures and tables, and selected text (up to 250 words, exclusive of the abstract) from the Contribution, for the Contributor's own teaching purposes, or for incorporation within another work by the Contributor that is made part of an edited work published (in print or electronic format) by a third party, or for presentation in electronic format on an internal computer network or external website of the Contributor or the Contributor's employer.

5. The right to include the Contribution in a compilation for classroom use (course packs) to be distributed to students at the Contributor's institution free of charge or to be stored in electronic format in datarooms for access by students at the Contributor's institution as part of their course work (sometimes called "electronic reserve rooms") and for in-house training programs at the Contributor's employer.

D. **CONTRIBUTIONS OWNED BY EMPLOYER**

1. If the Contribution was written by the Contributor in the course of the Contributor's employment (as a "work-made-for-hire" in the course of employment), the Contribution is owned by the company/employer which must sign this Agreement (in addition to the Contributor's signature), in the space provided below. In such case, the company/employer hereby assigns to Wiley, during the full term of copyright, all copyright in and to the Contribution for the full term of copyright throughout the world as specified in paragraph A above.

2. In addition to the rights specified as retained in paragraph B above and the rights granted back to the Contributor pursuant to paragraph C above, Wiley hereby grants back, without charge, to such company/employer, its subsidiaries and divisions, the right to make copies of and distribute the published Contribution internally in print format or electronically on the Company's internal network. Upon payment of Wiley's reprint fee, the institution may distribute (but not resell) print copies of the published Contribution externally. Although copies so made shall not be available for individual re-sale, they may be included by the company/employer as part of an information package included with software or other products offered for sale or license. Posting of the published Contribution by the institution on a public access website may only be done with Wiley's written permission, and payment of any applicable fee(s).

E. **GOVERNMENT CONTRACTS**

In the case of a Contribution prepared under U.S. Government contract or grant, the U.S. Government may reproduce, without charge, all or portions of the Contribution and may authorize others to do so, for official U.S. Government purposes only, if the U.S. Government contract or grant so requires. (U.S. Government Employees: see note at end.)

F. **COPYRIGHT NOTICE**

The Contributor and the company/employer agree that any and all copies of the Contribution or any part thereof distributed or posted by them in print or electronic format as permitted herein will include the notice of copyright as stipulated in the Journal and a full citation to the Journal as published by Wiley.

G. **CONTRIBUTOR'S REPRESENTATIONS**

The Contributor represents that the Contribution is the Contributor's original work. If the Contribution was prepared jointly, the Contributor agrees to inform the co-Contributors of the terms of this Agreement and to obtain their signature to this Agreement or their written permission to sign on their behalf. The Contribution is submitted only to this Journal and has not been published before, except for "preprints" as permitted above. (If excerpts from copyrighted works owned by third parties are included, the Contributor will obtain written permission from the copyright owners for all uses as set forth in Wiley's permissions form or in the Journal's Instructions for Contributors, and show credit to the sources in the Contribution.) The Contributor also warrants that the Contribution contains no libelous or unlawful statements, does not infringe upon the rights (including without limitation the copyright, patent or trademark rights) or the privacy of others, or contain material or instructions that might cause harm or injury.

CHECK ONE:

[____] Contributor-owned work

Contributor's signature ____________________ Date ________

Type or print name and title ____________________

Co-contributor's signature ____________________ Date ________

Type or print name and title ____________________

ATTACHED ADDITIONAL SIGNATURE PAGE AS NECESSARY

[____] Company/Institution-owned work
(made-for-hire in the
course of employment)

Company or Institution (Employer-for-Hire) ____________________ Date ________

Authorized signature of Employer ____________________ Date ________

[____] U.S. Government work

Note to U.S. Government Employees

A contribution prepared by a U.S. federal government employee as part of the employee's official duties, or which is an official U.S. Government publication is called a "U.S. Government work," and is in the public domain in the United States. In such case, the employee may cross out Paragraph A.1 but must sign and return this Agreement. If the Contribution was not prepared as part of the employee's duties or is not an official U.S. Government publication, it is not a U.S. Government work.

[____] U.K. Government work (Crown Copyright)

Note to U.K. Government Employees

The rights in a Contribution prepared by an employee of a U.K. government department, agency or other Crown body as part of his/her official duties, or which is an official government publication, belong to the Crown. In such case, Wiley will forward the relevant form to the Employee for signature.

WILEY
Publishers Since 1807

111 RIVER STREET, HOBOKEN, NJ 07030

Telephone Number: • Facsimile Number:

To: Christine Haller, Production Editor
Company: Cadmus Professional Communications
Phone: 800-238-3814 ext. 627
Fax: 717-738-9444

From:
Date:
Pages including this cover page:

Message:

Re:

tapraid5/zqz-qua/zqz-qua/zqz01105/zqz1361-05a | franklim | S=8 | 12/28/04 | 11:30 | Art: QUA-2004-0093 | Input-yyy(mek)

Memory Formulas for Perturbations in Time-Dependent Density Functional Theory

NEEPA T. MAITRA

Department of Physics and Astronomy, Hunter College of the City University of New York, New York, NY 10021

Received 13 October 2004; accepted 10 November 2004
Published online in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.20465

ABSTRACT: Exact time-dependent density functionals depend on both the entire history of the density and the initial wave function. Recently we have shown that the two effects are entangled by an exact condition that should be useful as a test in building accurate memory-dependent functionals. Here we consider this condition for small perturbations and derive an exact relation connecting the exchange-correlation kernel with initial-state derivatives. We discuss other exact conditions on the initial-state derivatives which shed some light on the elusive memory-dependence in time-dependent density functional theory. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 102: 000–000, 2005

Key words: density functional theory; time-dependent; memory; exchange-correlation; linear response

1. Introduction

Time-dependent density functional theory (TDDFT) is becoming increasingly popular for calculating excitation energies, spectra, and frequency-dependent polarizabilities, of atoms, molecules, clusters, and solids. Calculations of phenomena in intense fields, such as high harmonic generation and photoionization, are beginning to emerge. In his 1998 Nobel lecture [1], John Pople noted that density functional theories lead to lower cost and so a wider range of applicability than conventional wave function methods; he was, of course, cited for his development of computational methods in quantum chemistry, including density functional theory, for which his co-prizewinner, Walter Kohn, was recognized [2].

The time-dependent theory is based on the Runge–Gross theorem [3, 4], which states that, for a given initial state, there is a one-to-one mapping between the time-dependent density and the time-dependent potential that the electrons evolve in. This allows mapping of the interacting system to a fictitious system of noninteracting electrons, the

Correspondence to: N. T. Maitra; e-mail: nmaitra@hunter.cuny.edu

tapraid5/zqz-qua/zqz-qua/zqz01105/zqz1361-05a | franklim | S=8 | 12/28/04 | 11:30 | Art: QUA-2004-0093 | Input-yyy(mek)

Kohn–Sham (KS) system, which has the same density as the interacting problem but is much easier to solve. The KS electrons evolve in a one-body potential that is the sum of external, Hartree, and exchange-correlation contributions, $v_S(\mathbf{r}t) = v_{ext}(\mathbf{r}t) + v_H(\mathbf{r}t) + v_{XC}(\mathbf{r}t)$. One may extract all properties of the time-dependent interacting system from the KS system, once the relevant functionals are known or well approximated. Although, in principle, the theory is exact, in particular the exchange-correlation potential $v_{XC}[n, \Psi_0, \Phi_0](\mathbf{r}t)$ as a functional of the density, the interacting initial state, and the KS initial state must in practice be approximated. TDDFT has been most widely applied in the linear response regime [5, 6], giving rise to hundreds of calculations of excitation energies and oscillator strengths (see, e.g., Refs. [4, 7] for many references).

Almost all calculations utilize an adiabatic approximation for the exchange-correlation potential at time t. For the linear response case, when one perturbs an initial ground state of density n, the approximation for the exchange-correlation kernel, $f_{XC}[n](\mathbf{r}, \mathbf{r}', t - t') = \delta v_{XC}[n](\mathbf{r}t)/\delta n(\mathbf{r}', t')$ is completely local in time—its Fourier transform to the frequency domain is independent of frequency. (In linear response there is no initial-state dependence, since, by the Hohenberg–Kohn theorem [8], an initial ground state is completely determined by its density.) The exact exchange-correlation potential at time t, however, depends on the entire history of the density $n(t')$ for $t' < t$ as well as on the interacting initial state $\Psi(0)$, and KS initial state $\Phi(0)$ [9]. In Ref. [10], we showed that these two memory effects (history dependence and initial-state dependence) are intricately connected and discussed an exact condition that the exchange-correlation potential must satisfy:

$$v_{XC}[n_{t'}, \Psi(t'), \Phi(t')](\mathbf{r}t) = v_{XC}[n_0, \Psi(0), \Phi(0)](\mathbf{r}t) \quad (1)$$

for $t > t'$, where the subscript on the density indicates the start time, i.e., the density is undefined at times earlier than the value of the subscript. For $t \geq t'$, $n_{t'}(t) = n_0(t)$. The initial-state arguments on the left-hand side (lhs) are the wave functions evolved from $\Psi(0)$, $\Phi(0)$ at time t' under the interacting and KS Hamiltonians, respectively. As discussed in Ref. [10], this relation interchanges initial-state dependence for history dependence. It can be used as a challenging test for approximate candidate functionals, as discussed in detail in Ref. [10]. Equation (1) also suggests how the need for initial-state dependence can be eliminated if an external potential can be found in which the initial state Ψ_0 evolves backward in time to a nondegenerate ground state; one can trade in the initial-state dependence for dependence along the "pseudo-prehistory" of the density from this earlier time to the true initial time (assuming noninteracting v-representability during the pseudo-prehistory [11]). There are many interesting consequences of this relation for TDDFT, especially for descriptions of states far from the ground state [10], as in quantum control problems.

Consider now applying formula (1) in the linear response regime, where an initial ground state at $t = 0$, of density $\bar{n}(\mathbf{r})$, is perturbed by a time-dependent potential $v_{ext}(\mathbf{r}t)$, giving rise to an evolving density $n(\mathbf{r}t) = \bar{n}(\mathbf{r}) + \delta n(\mathbf{r}t)$. The memory formula then yields an expression for the exchange-correlation kernel entirely in terms of initial-state dependence {Eq. (7) of Ref. [10]}:

$$\sum_\alpha \int d^3r_1 \left.\frac{\delta v_S[n_{t'}, \Phi_{t'}](\mathbf{r}t)}{\delta \phi_{t',\alpha}(\mathbf{r}_1)}\right|_{(\bar{n},\bar{\Phi}[\bar{n}])} \delta\phi_{t',\alpha}(\mathbf{r}_1)$$
$$- \int dx_1 \cdots dx_N \left.\frac{\delta v_{ext}[n_{t'}, \Psi_{t'}](\mathbf{r}t)}{\delta \Psi_{t'}(x_1 \cdots x_N)}\right|_{(\bar{n},\bar{\Phi}[\bar{n}])} \delta\Psi_{t'}(x_1 \cdots x_N)$$
$$+ \text{c.c.} = \int d^3r_1 \int_0^{t'} dt_1 f_{XC}[\bar{n}](\mathbf{r}\mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1),$$
$$0 < t' < t, \quad (2)$$

where the variables $x_i = (\mathbf{r}_i, \sigma_i)$ represent spatial and spin coordinates, $\delta\phi_{t',\alpha} = \delta\phi_\alpha(t') = \phi_\alpha(t') - \bar{\phi}_\alpha[\bar{n}]$ represent the deviations at time t' of the spin–orbitals of the KS Slater determinant away from the ground-state values, and $\delta\Psi$ is similarly the deviation of the interacting state away from its ground state.

The derivation and meaning of this equation is subtle, as it involves partial functional derivatives with respect to the initial state and with respect to the density: these variables are not completely independent because, for example, the initial state determines the initial density as well as its first time derivative (through the continuity equation), so care is needed in defining the variations, and what is held fixed in each functional derivative. In this article we discuss how to define the derivatives (Section 2), and give a detailed derivation of the memory formula for linear response in Section 3. In Section 4, we discuss other exact relations that the initial-state derivatives satisfy. In addition to being exact conditions that are useful in guiding the construction of accurate approximate functionals with memory, these equations shed some light on the elusive memory dependence in TDDFT.

2. Functional Variations under Initial State and Density Changes

General time-dependent functionals at time t depend on the history of the density $n(\mathbf{r}t')$ for all $t' < t$, as well as on the initial state Ψ_0 of the interacting system, and the initial state of the KS system Φ_0. Of particular interest is how the exchange-correlation potential functional depends on these three elements. We wish to formulate a description of how this changes under small perturbations of the initial states and density evolution.

The bulk of our initial discussion considers, for simplicity, the KS potential functional, $v_S[n; \Phi_0](\mathbf{r}t)$, that determines the evolution of the KS system; it is straightforward to formally generalize the results to the interacting case, and these results are stated. Consider first the simplest situation: the initial state is a ground state, so, by the Hohenberg–Kohn theorem, is itself a functional of its own density. Then, under a variation of the density that holds the initial state fixed, we have the usual definition of the inverse susceptibility,

$$v_S[\bar{n} + \delta n](\mathbf{r}t) = v_S[\bar{n}](\mathbf{r}) + \int_0^t dt_1 \int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1). \quad (3)$$

Here and following, a bar indicates that the wave function or density is a ground-state one. The susceptibility χ_S is a familiar object from linear response theory [5], where a small perturbation is made at time $t > 0$ to an initial ground state: in this situation there is no change in the density at the initial time, nor in its first time derivative at $t = 0$, since these are determined completely by the initial state, which is held fixed.

The first generalization to make is to drop the restriction on the initial state being a ground state. Then, still holding the initial state fixed, we write

$$v_S[n + \delta n, \Phi](\mathbf{r}t) = v_S[n, \Phi](\mathbf{r}t) + \int_0^t dt_1 \int d^3r_1 \chi_S^{-1}[n, \Phi](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1), \quad (4)$$

where

$$\chi_S^{-1}[n, \Phi](\mathbf{r}, \mathbf{r}_1, t - t_1) = \left.\frac{\delta v_S[n, \Phi](\mathbf{r}t)}{\delta n(\mathbf{r}_1, t_1)}\right|_{\Phi\ \mathrm{const}}. \quad (5)$$

When the initial state is a ground state of density $\bar{n}$, $\chi_S[n, \Phi](\mathbf{r}, \mathbf{r}', t)$ reduces to the familiar KS susceptibility of Eq. (3). In this sense, $\chi_S[n, \Phi]$ is a generalized susceptibility where we are restricted neither to initial ground states nor to ground-state densities. We note that this derivative describes changes in the potential due to density perturbations after time $t = 0$; it does not include changes in the density at the initial time, nor in its first time derivative at $t = 0$, since these are determined completely by the fixed initial state.

More generally, we wish to also consider how the potential changes when the initial state changes. This will immediately cause a change in the density: the initial state determines the initial density, through

$$n(\mathbf{r}0) = \sum_{\alpha=1}^{N} |\phi_\alpha(\mathbf{r})|^2 \quad (6)$$

and also its first time derivative, through the equation of continuity,

$$\dot{n}(\mathbf{r}0) = -i\nabla \cdot \sum_{\alpha=1}^{N} (\phi_\alpha(\mathbf{r})\nabla\phi_\alpha^*(\mathbf{r}) - \phi_\alpha^*(\mathbf{r})\nabla\phi_\alpha(\mathbf{r}))/2. \quad (7)$$

The spin–orbitals ϕ_α are those that make up the initial KS Slater determinant of the reference state Φ. This makes the issue of defining a response function with respect to the initial state much more subtle than that with respect to the density: we cannot, for example, vary the initial state while holding the density fixed. Moreover, the initial state affects even higher-order time derivatives of the density: for example, we cannot vary the initial state while holding just the second and higher derivatives of the density fixed, because the resulting density is unphysical, as shown in the Appendix. The initial state determines the zeroth and first-order time derivatives of the density uniquely, and places restrictions on the higher-order time derivatives. These restrictions arise from the requirement that the resulting evolving density must arise from evolving the initial state in a well-behaved, one-body potential, in a norm-conserving KS equation. One may attempt to define the partial derivative by choosing a particular solution to these restrictions, but it is certainly not a unique choice, nor is it simple to see if one can be selected on the basis of a physical reason.

Consider instead an extension of the functionals to a higher space in which the initial state and density are independent; the relations Eq. (6) and (7) are dropped. The true physical space forms a subspace of this, defined by the physically compatible $[n, \Phi_0]$ pairs where the density $n(t)$ arises from evolving the initial state Φ_0 in a well-behaved, one-body potential. Then, one can define partial functional derivatives where either the initial state or the density is held fixed, while the other variable is varied. Under a small variation of the initial state and density, we write

$$v_S[n + \delta n, \Phi_0 + \delta\Phi_0](\mathbf{r}t) = v_S[n, \Phi_0](\mathbf{r}t) + \int_0^t dt_1 \int d^3r_1 \chi_S^{-1}[n, \Phi](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1) + \sum_\alpha \int d^3r_1 \xi_{S,\alpha}[n, \Phi](\mathbf{r}, \mathbf{r}_1, t)\delta\phi_\alpha(\mathbf{r}_1) + \text{c.c.} \quad (8)$$

The two response functions, $\chi_S^{-1}[n, \Phi]$ and $\xi_{S,\alpha}[n, \Phi]$, are partial derivatives with respect to the density and initial state respectively, in the extended space. This is illustrated in Figure 1. F1

The initial-state derivative is thus defined as the change of the KS potential at times t when the initial state is varied on the extended space, holding the density variable fixed. The generalized susceptibility is defined as the change in the KS potential at time t when the density at time $t' > 0$ is varied, holding the initial state fixed. When evaluated on a physically compatible $[n, \Phi]$ pair, it reduces to the generalized susceptibility defined physically through Eq. (4). [Note that the susceptibility in the first term on the right-hand side (rhs) of Eq. (8) generally multiplies variations in the density and its first time derivative that are nonzero at the initial time, so we cannot use the definition in Eq. (4) to associate that term on its own to a physically defined change in potential.]

The discussions above are easily generalized to the interacting system, where variations of v_{ext} are considered instead, and the initial state is the fully interacting wave function $\Psi(x_1 \cdots x_N)$. The analogues of Eqs. (3), (4), and (8) are

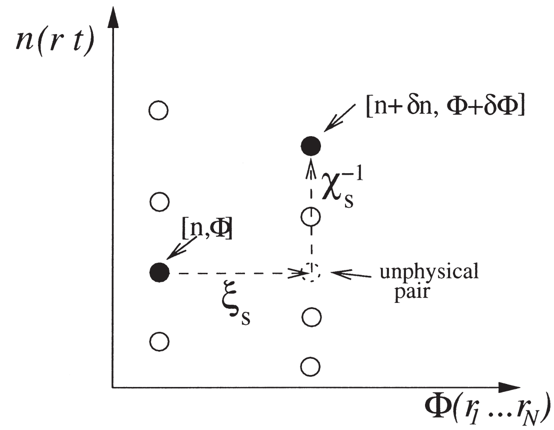

FIGURE 1. Cartoon of a general variation of the initial state and density, in the extended space. Each initial state gives rise to a class of physical density evolutions indicated by the circles. The process that gives the change in KS potential when a small change is made in the initial state, $\Phi \rightarrow \Phi + \delta\Phi$, and the density evolution $n(t) \rightarrow n(t) + \delta n(t)$, can be described by two response functions, connecting through an unphysical initial-state–density pair, as described in the text.

$$v_{\text{ext}}[\bar{n} + \delta n](\mathbf{r}t) = v_{\text{ext}}[\bar{n}](\mathbf{r}t) + \int_0^t dt_1 \int d^3r_1 \chi^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1), \quad (9)$$

$$v_{\text{ext}}[n + \delta n, \Psi](\mathbf{r}t) = v_{\text{ext}}[n, \Psi](\mathbf{r}t) + \int_0^t dt_1 \int d^3r_1 \chi^{-1}[n, \Psi](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1), \quad (10)$$

and,

$$v_{\text{ext}}[n + \delta n; \Psi + \delta\Psi](\mathbf{r}t) = v_{\text{ext}}[n, \Psi](\mathbf{r}t) + \int dx_1 \cdots dx_N \xi[n, \Psi](\mathbf{r}, x_1 \cdots x_N, t)\delta\Psi(x_1 \cdots x_N) + \text{c.c.} + \int_0^t dt_1 \int d^3r_1 \chi^{-1}[n, \Psi](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1). \quad (11)$$

It is the $\xi_{S,\alpha}[n, \Phi](\mathbf{r}, \mathbf{r}_1, t)$ and $\xi[n, \Psi](\mathbf{r}, x_1 \cdots x_N, t)$ that correspond to the initial-state derivatives in Eq. (2). We shall return to this now.

tapraid5/zqz-qua/zqz-qua/zqz01105/zqz1361-05a | franklim | S=8 | 12/28/04 | 11:30 | Art: QUA-2004-0093 | Input-yyy(mek)

3. Derivation of Memory Formula in Linear Response

The memory formula for the KS potential is [10]

$$v_S[n_{t'}, \Phi(t')](\mathbf{r}t) = v_S[n_0, \Phi(0)](\mathbf{r}t), \quad 0 < t' < t \quad (12)$$

and that for the external potential just replaces v_S with v_{ext} and the KS initial state Φ with the interacting initial state, Ψ. We shall show that expressing the exchange-correlation kernel [5] as

$$f_{XC}[\bar{n}](\mathbf{r}, \mathbf{r}', t) = \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}', t) - \chi^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}', t) - \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|}, \quad (13)$$

where $\bar{n}(\mathbf{r})$ is a ground-state density, allows us to obtain Eq. (2): one subtracts variations of the memory formula for the external potential from that for the KS potential in the linear response situation. Being completely local in time, the Hartree kernel (the third term on the rhs) plays no role for memory: for example, writing $v_S = v_{ext} + v_H + v_{XC}$ on either side of Eq. (12), v_H cancels out on each side of the formula.

We consider the KS memory formula, Eq. (12), when we turn on a weak perturbation $\delta v_S(\mathbf{r}t)$ at time $t = 0$ on a ground state, as in the linear response situation. To first order in the perturbation, the density evolves as $n_0(t) = \bar{n} + \delta n(t)$, with $n_0(0) = \bar{n}$. The memory formula becomes, for this case,

$$v_S[n_{t'}, \Phi(t')](\mathbf{r}t) = v_S[n_0](\mathbf{r}t), \quad 0 < t' < t, \quad (14)$$

with $n_{t'}(t) = n_0(t)$, $t \geq t'$ and undefined otherwise. There is no initial-state dependence on the rhs, thanks to the Hohenberg–Kohn theorem [8], since we begin at $t = 0$ in a ground state, $\Phi(0) = \bar{\Phi}[\bar{n}]$, with $\bar{n} = n_0(0)$. The initial state on the lhs is determined by $\Phi(t') = U_S(t')\Phi(0) = e^{-i\bar{E}_0 t}\bar{\Phi}_0 + \delta\Phi(t)$ where $U_S(t)$ is the unitary time-evolution operator for the KS system and $\bar{E}_0$ is the expectation value of the KS Hamiltonian in the unperturbed KS state.

We expand each side of Eq. (14) about the unperturbed ground-state value. The rhs gives the familiar linear response result:

$$v_S[n_0](\mathbf{r}t) = v_S[\bar{n}](\mathbf{r}) + \int_0^t dt_1 \int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1 t_1), \quad (15)$$

where χ_S is the usual dynamic KS susceptibility of Eq. (2) and $\delta n(\mathbf{r}_1 t_1) = n(\mathbf{r}_1 t_1) - \bar{n}(\mathbf{r}_1)$.

The initial state on the lhs of Eq. (14) is not a ground state. Applying the general formula, Eq. (8), we get

$$v_S[n_{t'}, \Phi(t')](\mathbf{r}t) = v_S[\bar{n}](\mathbf{r}) + \int d^3r_1 \sum_\alpha \xi_{S,\alpha}[\bar{n}_{t'}](\mathbf{r}, \mathbf{r}_1, t - t')\delta\phi_\alpha(\mathbf{r}_1, t') + \int d^3r_1 \int_{t'}^t dt_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1) + \text{c.c.} \quad (16)$$

Comparing with Eq. (15), we get

$$\int_0^{t'} dt_1 \int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1) = \sum_\alpha \int d^3r_1 \xi_{S,\alpha}[\bar{n}_{t'}](\mathbf{r}, \mathbf{r}_1, t - t')\delta\phi_\alpha(\mathbf{r}_1, t') + \text{c.c.} \quad (17)$$

for $0 < t' < t$. The integral on the lhs contains only the history of the density up to time t'; this is the time at which the evolved wave function is input on the rhs, demonstrating the interchange of the two memory effects, as in the general formula Eq. (1).

Repeating the calculation for the interacting system, where we consider variations of the external potential, we obtain

$$\int_0^{t'} dt_1 \int d^3r_1 \chi^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1) = \int dx_1 \cdots dx_N \xi[\bar{n}_{t'}](\mathbf{r}, x_1 \cdots x_N, t - t')\delta\Psi(x_1 \cdots x_N, t') + \text{c.c.} \quad (18)$$

for $0 < t' < t$. Finally, using Eq. (13), we subtract Eq. (18) from Eq. (17), and obtain the result for the exchange-correlation kernel:

$$\int_0^{t'} dt_1 \int d^3r_1 f_{XC}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1, t_1)$$
$$= \sum_\alpha \int d^3r_1 \xi_{S,\alpha}[\bar{n}_{t'}](\mathbf{r}, \mathbf{r}_1, t - t')\delta\phi_\alpha(\mathbf{r}_1, t')$$
$$- \int dx_1 \cdots dx_N \xi[\bar{n}_{t'}](\mathbf{r}, x_1 \cdots x_N, t - t')\delta\Psi(x_1 \cdots x_N, t') + \text{c.c.} \quad (19)$$

for $0 < t' < t$. This ends our proof of Eq. (2).

As predicted, the Hartree kernel does not appear; the time delta-function in Eq. (13) does not contribute when $t' < t$. It is, however, instructive to see what happens if we allow t' to equal t. The Hartree kernel then must also be subtracted from Eq. (17), and yields a new term—$\int d^3r_1 \delta n(\mathbf{r}_1, t)/|\mathbf{r} - \mathbf{r}_1|$—on the rhs of Eq. (19). This is just the Hartree response potential at time t to a density change $\delta n(\mathbf{r}t)$. The lhs becomes, by definition of the kernel, just the change in the exchange-correlation potential when the density is perturbed as $\delta n(\mathbf{r}t_1)$ for times $0 < t_1 < t$. Identifying the initial-state derivative terms in Eq. (19) as $\delta v_S(\mathbf{r}t)$ and $\delta v_{ext}(\mathbf{r}t)$ respectively, then, at $t' = t$, Eq. (19) simply becomes the statement $\delta v_{XC}(\mathbf{r}t) = \delta v_S(\mathbf{r}t) - \delta v_{ext}(\mathbf{r}t) - \delta v_H(\mathbf{r}t)$.

4. Other Exact Conditions

We now discuss two more examples of initial-state dependence in the perturbative regime and their implications for the properties of the initial-state derivative. The examples lead to exact conditions that it must satisfy.

Consider expressing the difference in two nearby ground-state potentials. In this case, the change in the "initial" state is from one ground state $\bar{\Phi}$ to another $\overline{\Phi + \delta\Phi}$, while the density change is constant in time, from $\bar{n}$ (corresponding to $\bar{\Phi}$) to $\overline{n + \delta n}$. (Here and following, a bar indicates that the wave function or density is a ground-state one.) Usually the difference in the KS potentials is described by the static susceptibility, Eq. (20). We first note that the time integral of the usual KS susceptibility $\chi_S[\bar{n}](\mathbf{r}, \mathbf{r}', t)$ is the static susceptibility $\chi_S[\bar{n}](\mathbf{r}, \mathbf{r}')$ of ground-state theory, describing the difference in the ground-state potentials of two slightly different ground states:

$$v_S[\overline{n + \delta n}](\mathbf{r}) = v_S[\bar{n}](\mathbf{r}) + \int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1)\delta n(\mathbf{r}_1), \quad (20)$$

where

$$\chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1) = \frac{\delta v_S[\bar{n}](\mathbf{r})}{\delta n(\mathbf{r}_1)} = \int_0^\infty dt \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t). \quad (21)$$

Now, using Eq. (8), we obtain an expression in terms of the initial-state derivatives:

$$\int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1)\delta n(\mathbf{r}_1) = v_S[\overline{n + \delta n}](\mathbf{r}) - v_S[\bar{n}](\mathbf{r})$$
$$= \int d^3r_1 \delta n(\mathbf{r}_1)\left(\int d^3r_2 \sum_\alpha \xi_{S,\alpha}[\bar{n}](\mathbf{r}, \mathbf{r}_2, t) \frac{\delta\phi_\alpha(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)} + \text{c.c.}\right.$$
$$\left. + \int_0^t dt_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\right). \quad (22)$$

Here we have expressed the variation in the ground-state orbitals in terms of the variation in the ground-state density. The time dependence of the initial-state derivative term $\xi_{S,\alpha}[\bar{n}](\mathbf{r}, \mathbf{r}', t)$ must be such to cancel that of the integrated dynamic susceptibility in this case since the lhs is time-independent. This example gives an exact condition, Eq. (22), that the KS initial-state derivative must satisfy.

For the interacting system, the analogous exact condition is

$$\int d^3r_1 \chi^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1)\delta n(\mathbf{r}_1)$$
$$= \int dx_1 \cdots x_N \xi[\bar{n}](\mathbf{r}, x_1 \cdots x_N, t)\delta\bar{\Psi}(x_1 \cdots x_N) + \text{c.c.}$$
$$+ \int d^3r_1 \int_0^t dt_1 \chi^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1, t - t_1)\delta n(\mathbf{r}_1). \quad (23)$$

Equations (22) and (23) express the static susceptibility of ground-state theory in terms of initial-state dependence and the dynamic susceptibility: they are exact conditions that the initial-state derivatives must satisfy. Noting that the lhs is time-independent, the time dependence of the initial-state derivative around a ground state must be such to exactly cancel out the time dependence of the time-integrated dynamic susceptibility. At $t = 0$ the potential difference, interpreted as being due to a sudden shift in the ground state, is given entirely by initial-state dependence:

$$v_S[\overline{n + \delta n}](\mathbf{r}) - v_S[\bar{n}](\mathbf{r}) = \int d^3r_1 \chi_S^{-1}[\bar{n}](\mathbf{r}, \mathbf{r}_1)\delta n(\mathbf{r}_1)$$
$$= \int d^3r_1 \delta n(\mathbf{r}_1) \sum_\alpha \int d^3r_2 \xi_{S,\alpha}[\bar{n}]$$
$$\times (\mathbf{r}, \mathbf{r}_2, 0) \frac{\delta\bar{\phi}_\alpha[\bar{n}](\mathbf{r}_2)}{\delta\bar{n}(\mathbf{r}_1)} + \text{c.c.} \quad (24)$$

On the other hand, in the limit that $t \to \infty$, the initial-state derivative term must vanish. Using Eq. (21), we see that in the limit that $t \to \infty$, the entire potential difference in Eq. (22) [or Eq. (23)] becomes a history effect. So

$$\int d^3r_1 \delta n(\mathbf{r}_1) \sum_\alpha \xi_{S,\alpha}[\bar{n}](\mathbf{r}, \mathbf{r}_2, t \to \infty) \frac{\delta\bar{\phi}_\alpha[\bar{n}](\mathbf{r}_2)}{\delta\bar{n}(\mathbf{r}_1)} = 0. \quad (25)$$

[Equations (24) and (25) are given for the KS system, but it is simple to see how they generalize to the interacting one.]

The equations [Eqs. (22), (23), (24), and (25)] tell us exactly what the initial-state derivative around a ground state must satisfy in terms of the static and dynamic susceptibilities, for the KS system [Eq. (22)] and the interacting one [Eq. (23)]. They display the entanglement of history dependence and initial-state dependence clearly, since the same ground-state potential can be expressed either completely as an initial-state perturbation, a history dependence, or as a mixture of the two.

The vanishing of the initial-state derivative term in the limit that $t \to \infty$ is not generally true: for example, when the initial-state deviation is not a ground-state one (even when the reference state is a ground state), the system never forgets its initial state. We can show that the initial-state derivative in this case is not zero when $t \to \infty$ by the following example.

We consider the situation of two states that evolve with the same density for all time, but begin in two different initial states. Their potentials differ: an example of this for two noninteracting electrons was considered in Refs. [9] and [12]. In that example, the reference wave function Φ was the (real-valued) ground state of two same-spin electrons in a simple 1D harmonic oscillator potential $v_S(x)$ at all times: both the density and the potential were static. A different wave function $\Phi + \delta\Phi$ (also real) was then found at $t = 0$ that reproduced the initial density and its first time derivative (zero) at the initial time, and the corresponding potential $v_S[\bar{n}, \Phi + \delta\Phi](x0)$ was calculated at $t = 0$. The difference between the reference and alternative wave functions depended on a parameter that could be made arbitrarily small. In terms of our initial-state derivative, we have

$$v_S[\bar{n}, \Phi + \delta\Phi](xt) = v_S[\bar{n}, \Phi](x) + \sum_\alpha \int dx_1 \xi_{S,\alpha}[\bar{n}, \Phi](x, x_1, t)\delta\phi_\alpha(x_1). \quad (26)$$

If, as $t \to \infty$, the initial-state term vanished, then $v_S[\bar{n}, \Phi + \delta\Phi](x, t) \to v_S[\bar{n}, \Phi](x)$ in that limit. That would mean that the wave function evolving in the alternative potential approaches the reference wave function: one can show that for a single Slater determinant (and other cases too), a constant density in a constant potential implies that the state is an eigenstate of that potential. This would mean that the wave function that $\Phi + \delta\Phi$ has evolved to in the potential $v_S[\bar{n}, \Phi + \delta\Phi](x, t)$ must approach the eigenstate Φ in the infinite time limit. However, that is a violation of the Runge–Gross theorem: if one reversed the evolution from the $t \to \infty$ limit, one would have two wave functions, beginning with the same initial state, evolving in two (eventually) different potentials but keeping the same density for all times. Therefore, the initial-state derivative term in Eq. (26) cannot vanish in the $t \to \infty$ limit. In summary, in this limit, the initial-state term around a ground state vanishes when the variation is a ground-state one [Eq. (25)] but not in general.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund and to the Research Foundation of CUNY for postal support of this research. The author thanks the anonymous referee for very useful comments, and acknowledges useful discussions with Kieron Burke during the early stages of this work.

References

1. Pople, J. A. Rev Mod Phys 1999, 71, 1267.
2. Kohn, W. Rev Mod Phys 1999, 71, 1253.
3. Runge, E.; Gross, E. K. U. Phys Rev Lett 1984, 52, 997.
4. Marques, M. A. L.; Gross, E. K. U. Ann Rev Phys Chem 2004, 55, 427.
5. Petersilka, M.; Gossmann, U. J.; Gross, E. K. U. Phys Rev Lett 1996, 76, 1212.
6. Casida, M. E. In Seminario, J. M., Ed. Recent Developments and Applications in Density Functional Theory; Elsevier: Amsterdam, 1996.
7. Maitra, N. T.; Burke, K.; Appel, H.; Gross, E. K. U.; van Leeuwen, R. In Sen, K. D., Ed. Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of Robert Parr; World Scientific: Singapore, 2002.
8. Hohenberg, P.; Kohn, W. Phys Rev B 1964, 136, 864.
9. Maitra, N. T.; Burke, K. Phys Rev A 2001, 63, 042501; 64, 039901 (E).
10. Maitra, N. T.; Burke, K.; Woodward, C. Phys Rev Lett 2002, 89, 023002.
11. van Leeuwen, R. Phys Rev Lett 1999, 82, 3863.
12. Holas, A.; Balawender, R. Phys Rev A 2002, 65, 034502.

Appendix

In this Appendix, we show the difficulties in attempting to define an initial-state derivative while remaining only within the physical space. As discussed in the text, the physical space is that where the initial state is compatible with the density evolution it is paired with: there exists a one-body well-behaved potential in which the initial state evolves so as to produce the time-evolving density.

Consider the change in $v_S(\mathbf{r}t)$ when the initial state changes from Φ to $\Phi + \delta\Phi$ and the density changes from $n(\mathbf{r}t)$ to $n(\mathbf{r}t) + \delta n(\mathbf{r}t)$. To retain the generalized susceptibility as the response function describing density changes, we need to break up the evolution into two steps: (i) the first must have the initial-state change (and consequently the initial density and its first time derivative) and (ii) the second must have no change in the initial state, and includes density changes only after $t > 0$. [See discussion in the text following Eq. (4).] The second step may then be captured by the generalized susceptibility of Eq. (4), and it remains to find a response function for the first step.

Notice that, in the first step, only the changes in the initial density and its first time derivative are completely specified. The simplest attempt to define an initial-state derivative for the first step is one where the initial density and its first time derivative may change, but all higher-order derivatives $d^k n(0)/dt^k$, $k \geq 2$, evaluated at $t = 0$, are held fixed: thus this derivative covers all variations not covered by the generalized susceptibility in Eq. (4). We may call the density defined in this way an "intermediate" density, since it will, in the second step, be corrected to the new density of interest, $n + \delta n$, through the susceptibility. It is important to note that this initial-state derivative includes nonzero density variations at all times, $\delta n(\mathbf{r}t) = \delta n(\mathbf{r}0) + t\delta\dot{n}(\mathbf{r}0)$, where $\delta n(\mathbf{r}0)$ and $\delta\dot{n}(\mathbf{r}0)$ are determined by the change in the initial state. We will now show that this choice leads to an unphysical density.*

Let $n(\mathbf{r}t)$ denote the density evolving from the reference initial state Φ and $\tilde{n}(\mathbf{r}t)$ denote the intermediate density: so

$$\tilde{n}(t) = n(t) + (\tilde{n}(0) - n(0)) + t(\dot{\tilde{n}}(0) - \dot{n}(0)). \tag{27}$$

Here $n(0)$ and $\dot{n}(0)$ are determined by the reference Φ, and $\tilde{n}(0)$ and $\dot{\tilde{n}}(0)$ are determined by the new initial state $\Phi + \delta\Phi$, as in Eqs. (6) and (7). We now argue that although Eq. (27) satisfies global charge conservation, locally the charge is unbounded. To see why, integrate Eq. (27) over some finite region. The lhs is the charge contained in that region at time t, in the intermediate evolution. Assuming that the initial states yield an initial current entering that region that is nonzero, then the last term in Eq. (27) grows or decreases linearly as a function of time, without bound. This implies that the charge in that region grows or decreases without bound, which is impossible in any physical evolution. [If the region is taken to be the entire space, then total charge is in fact conserved: the last term in Eq. (27) integrated over all space is zero at all times, since no currents can enter or leave the infinite region. For every region in which the charge grows without bound, there is another region in which charge correspondingly decreases without bound so that over the whole space, the charge remains constant.]

*The author is grateful to the anonymous referee for pointing this out.

tapraid5/zqz-qua/zqz-qua/zqz01105/zqz1361-05a | franklim | S=8 | 12/28/04 | 11:30 | Art: QUA-2004-0093 | Input-yyy(mek)

The local violation of charge boundedness is a consequence of the fact that we are not entirely free to choose the second- and higher-order derivatives of the density evolution, given a fixed initial state. It is clear that the initial state entirely determines the initial density and its first time derivative but it also places conditions on all higher-order time derivatives of the density, because the density must evolve under a norm-conserving KS equation, in a well-behaved, one-body potential.

So, we may try to define an initial-state derivative for step (i), with a physically allowable intermediate density, by requiring it to satisfy such conditions. The problem is that it is not unique, and it is not clear whether a "natural choice" exists.