Manuscript Submission

Physical Review & Physical Review Letters

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User: "matthias_schmidt" < matthias.schmidt@uni-bayreuth.de >
Temporary ID: es2011jan19_018
Submission status: Submitted

- **Confirmation of submission**

Your cover letter:

```
JNL: pre
TEMPID: es2011jan19_018
RECVD: Wed Jan 19 03:25:07 2011
TITLE: Variational Principle of Classical Density Functional Theory via Levy's Constrained Search Method
FIRSTA_LAST: Dwandaru
FIRSTA_FIRST: Wipsar
FIRSTA_MIDDLE: Sunu Brams
FIRSTA_OTHER:
AUTHORS: Dwandaru, Wipsar Sunu Brams/Schmidt, Matthias/
CORRA_LAST: Schmidt
CORRA_FIRST: Matthias
CORRA_MIDDLE:
CORRA_OTHER:
EMAIL: matthias.schmidt@uni-bayreuth.de
ADDRESS: Theoretische Physik II
Physikalisches Institut
Universitaet Bayreuth
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Germany
PHONE: 011+49-921-55-3313
FAX: 011+49-921-55-2991
ART_TYPE: Regular Article
SEQUEL:
SECTION: E-1C
TYPE: TH
PACS1: 61.20.Gy
PACS2: 64.10.+h
PACS3: 05.20.Jj
PACS4:
NFIGS: 0
COLORFIGS: no,
EFIG: No figures
NTABLES: 0
COPY: STANDARD
LENGTHCHECK: 744 lines (6.2 pages)
REFCHECK: No errors detected
REFEREES: J.R. Henderson (Leeds), R. van Roij (Utrecht), R. Roth (Erlangen),
A.J. Archer (Loughborough), A.O.Parry (Imerial College), M. Oettel
(Mainz), P.Tarazona (Madrid)
```

and files

- levy.tex

were submitted to Physical Review E

By submitting this manuscript, the corresponding author certifies: - The paper represents original work of the listed authors. - The manuscript as presented accurately reflects the scientific results. - All of the authors made significant contributions to the concept, design, execution, or interpretation of the research study. - All those who made significant contributions were offered the opportunity to be listed as authors. - All of the listed authors are aware of and agree to the submission of this manuscript. - The manuscript has not been published, and is not now and will not be under consideration by another journal while it is considered here. - As part of the submission, the authors have provided any relevant information to the editors (e.g., information about recent relevant unpublished manuscripts by the authors). - The authors accept the established procedures for selecting manuscripts for publication.

If you will be leaving this browser session in a place where somebody else may use it after you, please logout when you are done.

Re: Levy Paper Submission

From: Matthias Schmidt (matthias.schmidt@uni-bayreuth.de)

To: wipsarian@yahoo.com

Cc: matthias.schmidt@uni-bayreuth.de

Date: Wednesday, 19 January 2011, 15:34 GMT+7

Dear Brams,

please find attached the submitted version of our fine 'Levy' paper. I hope that the referees will like it. I just sent the texfile to Phys.Rev.E. It will of course take a while untile we hear from them. It has been a great pleasure to work on this with you! -And we kept being productive right until the end!

I have started to work on the second paper (variational framework for dynamics) already. I went twice throught the introduction, and will now have to shorten the model section. I hope that revising this will not take too long and will keep you updated.

We had a nice talk yesterday by Andreas Schadschnieder (U Cologne). He mentioned that 2D particle hopping models are used to model pedestrian transport, i.e. people walking in all sorts of environments. This is maybe some motivation for your 2D investigation. If you have some time you could check Schadschnieder's papers.

All the best,
Matthias

On 18.01.2011, at 12:41, Brams Dwandaru wrote:

> Dear Matthias,
>
> I've read the latest Levy paper. I really like it.
>
> Please do submit it. Let me know if you have done so. Hopefully the process goes well.
>
> Do you want to go on to our second paper?

Best regards,
Brams

-- On **Mon, 17/1/11, Matthias Schmidt <*matthias.schmidt@uni-bayreuth.de*>** wrote:

> From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
> Subject: Re: Revised Levy Paper
> To: "Brams Dwandaru" <wipsarian@yahoo.com>
> Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
> Date: Monday, 17 January, 2011, 23:00
>
> Dear Brams.
>
> it is late and I have to go soon. I think we have done the best that we can with this
> paper. The latest proof-reading has improved and polished it quite considerably.
> I think that the paper is finished. If I have your OK I will go ahead and submit it
> to Phys. Rev. E! Please let me know!
> Thank yo u for all the work that went into this!
>
> All the best,
> Matthias
>
> On 17.01.2011, at 03:04, Brams Dwandaru wrote:
>
> > Dear Matthias,
> >
> > I've read the revised article. Overall it is very nice, clear, and easy to understand.
> >
> > I have small corrections, I think.
> >
> > 1. Page 7: In Eq. (16) v(r) should be inside the bracket, \rho(r) should be outside.
> > Below Eq. (16) third line \Omega_{v}[\rho].

Last line of Eq. (17) should be \Omega_{v}[\rho].

2. Page 8: I am not sure about this, may be I am wrong. Above Eq. (24), third line from below, you refer to Eq. (4). Eq. (4) is \Omega as a functional of f. Why Eq. (4)?

3. Page 12: End of Eq. (51) should be a full stop.

I also attached the above pages.

Please let me know if you have found other corrections.

Best regards,
Brams

--- On **Sat, 15/1/11, Matthias Schmidt <*matthias.schmidt@uni-bayreuth.de*>** wrote:

From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
Subject: Re: Revised Levy Paper
To: "Brams Dwandaru" <wipsarian@yahoo.com>
Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
Date: Saturday, 15 January, 2011, 23:48

Dear Brams,
I re-read it as well, and think it is in an excellent shape. What I still want to do is to go carefully step-by-step through all equations. (This will probably be the rest of my evening here.)
I think that we have done the best job that we could on this paper and that we are almost ready to submit. Still, please re-read it, as you write in your email. Then we exchange another email (soon) and then we submit, which is great!
Matthias

On 15.01.2011, at 09:45, Brams Dwandaru wrote:

Dear Matthias,

Thank you very much for your email. Thank you for sending me the revised version.

I've read the discussion and conclusion section. I think it is very nice and clear. I agree with what is written in this section.

And now I am reading the revised version of the article from the beginning.

I will keep in touch.

Best wishes,
Brams

--- On **Fri, 14/1/11, Matthias Schmidt <*matthias.schmidt@uni-bayreuth.de*>** wrote:

> From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
> Subject: Re: Levy Paper
> To: "Brams Dwandaru" <wipsarian@yahoo.com>
> Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
> Date: Friday, 14 January, 2011, 17:19
>
> Dear Brams,
>
> thank you for this detailed and very useful corrections. You did an excellent job!
> I agree with all points that you found and implemented those.
>
> 4. Page 10. Above eqn (36) should there be an 'an' before equality?
>
> I think not, is OK as is.
>
> 5. Page 11. Should there be a symbol of the total free energy for the LHS of (42), or just leave it as it is?

I left this away in order to save a symbol. Note that the canonical free energies have a roman letter F
(not calligraphic typesetting). I re-wrote the line above Eq.(42). I think is ok like this. Please re-check.

I attach the latest, re-vised version. I changed "equation" to "Eq." for Phys.Rev.E style. Please re-read.
And also, yes, please have a look at the conclusions as well.

Matthias

On 14.01.2011, at 08:11, Brams Dwandaru wrote:

> Dear Matthias,
>
> Thank you very much for your email.
>
> I've almost finish reading the draft. It is very very nice. I've attached scans of some pages that may (or not) be typos.
>
> 1. Page 5. Yes you are correct. RHS of eqn (10) should be f-f_{0}.
>
> 2. Page 8. RHS of eqn (28), the sum should be i = 1.
>
> 3. Page 9. Above eqn (30). Should it be 'inequality' ? LHS and RHS of eqn (34), \Gamma
> should be m.
>
> 4. Page 10. Above eqn (36) should there be an 'an' before equality? Or probably I am wrong. Should \rho(r') be \rho(r) on the LHS of eqn (39) for consistency with similar expression in other parts of the article?
>
> 5. Page 11. Should there be a symbol of the total free energy for the LHS of (42), or just leave it as it is?

6. Page 13. The comma on eqn (60) should be moved after the bracket.

I am reading the discussion and conclusion section. I will get back to you as soon as possible.

Thank you for the forwarding email from Bob. I've sent him a reply and did what he wanted me to do.

I will keep in touch.

Best regards,
Brams

--- On **Thu, 13/1/11, Matthias Schmidt <*matthias.schmidt@uni-bayreuth.de*>** wrote:

> From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
> Subject: Re: Levy Paper
> To: "Brams Dwandaru" <wipsarian@yahoo.com>
> Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
> Date: Thursday, 13 January, 2011, 19:53
>
> Dear Brams,
>
> can you check the left hand side of the inequality (10). I think this should be f-f_0, and not the other way round as is given in the present version. Can you please check? One has to derive it from (9) of course. There are no bad consequences, as in either case this vanishes. Please have a look.
>
> Matthias

<levy1.pdf><levy2.pdf><levy3.pdf><levy4.pdf><levy5.pdf><levy6.pdf>

<levy7.pdf><levy8.pdf><levy9.pdf>

levy_2011_01_19.tex
38kB

levy_2011_01_19.pdf
149.7kB

Fwd: Editorial Acknowledgment EA10780 Dwandaru

From: Matthias Schmidt (matthias.schmidt@uni-bayreuth.de)

To: wipsarian@yahoo.com

Cc: matthias.schmidt@uni-bayreuth.de

Date: Thursday, 20 January 2011, 21:18 GMT+7

Dear Brams,
please see below FYI.
Matthias

Begin forwarded message:

> From: pre@aps.org
> Date: 20. Januar 2011 14:58:48 MEZ
> To: matthias.schmidt@uni-bayreuth.de
> Subject: Editorial Acknowledgment EA10780 Dwandaru
> Reply-To: pre@aps.org
>
> Re: EA10780
> Variational principle of classical density functional theory via
> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
>
> Dear Dr. Schmidt,
>
> The editors acknowledge receipt of this manuscript on 19 January 2011
> and are considering it as a Regular Article in Physical Review E.
> When sending correspondence regarding this manuscript please refer to
> the code number EA10780.
>
> We understand your submission of this manuscript to certify the
> following:
>
> - The paper represents original work of the listed authors.
>
> - The manuscript as presented accurately reflects the scientific

> results.
>
> - All of the authors made significant contributions to the concept,
> design, execution, or interpretation of the research study.
>
> - All those who made significant contributions were offered the
> opportunity to be listed as authors.
>
> - All of the listed authors are aware of and agree to the submission
> of this manuscript.
>
> - The manuscript has not been published, and is not now and will not
> be under consideration by another journal while it is considered here.
>
> - As part of the submission, the authors have provided any relevant
> information to the editors (e.g., information about recent relevant
> unpublished manuscripts by the authors).
>
> - The authors accept the established procedures for selecting
> manuscripts for publication.
>
> Please check the attached information and send us any corrections.
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> System at http://authors.aps.org/STATUS/.
>
> Yours sincerely,
>
> Joanna Popadiuk
> Assistant Editor
> Physical Review E
> Email: pre@ridge.aps.org
> Fax: 631-591-4141
> http://pre.aps.org/
>
>
> Please verify the following information and notify the Editorial
> office of any corrections:
>
> Code number: EA10780
> Journal: PRE Regular Article
> Received: 19 January 2011
> Section: Statistical physics
>

> PACS: 64.10.+h 61.20.Gy 05.20.Jj
>
> Complete PACS listings can be obtained via
> http://publish.aps.org/PACS/pacsgen.html
>
> Address:
>
> Dr. Matthias Schmidt
> Theoretische Physik II
> Physikalisches Institut
> Universitaet Bayreuth
> D-95440 Bayreuth
> GERMANY
>
> Email: matthias.schmidt@uni-bayreuth.de
> Phone: 011+49-921-55-3313
> Fax: 011+49-921-55-2991
>
> Title: Variational principle of classical density functional theory
> via Levy's constrained search method
>
> Collaboration:
>
> 2 Author(s):
>
> Wipsar Sunu Brams Dwandaru, Matthias Schmidt
>
> FORMS AND MEMOS:
>
> Please see the following:
>
> http://forms.aps.org/author/rvwstndrds-au-pre.pdf
> Physical Review E, review standards

Fwd: Your_manuscript EA10780 Dwandaru

From: Matthias Schmidt (matthias.schmidt@uni-bayreuth.de)

To: wipsarian@yahoo.com

Cc: matthias.schmidt@uni-bayreuth.de

Date: Thursday, 3 March 2011, 15:48 GMT+7

Dear Brams,

please see below the email that I received from Phys.Rev.E about our paper. Maybe you want to go scroll down and first read what the referees say, before you go on reading what I think?

Plase scroll down!

Referee A did not get our message and we have to explain to him what our paper is about. Referee B is very nice and say kind things! Clearly Referee B liked our paper.

We will try and "fight" Referee A and convince him to make a positive judgment. This requires some thought on our side. I have to say that I am not very eager to go into all the details that he lays out in his report. Let us see, please read the reports carefully.

All the best,
Matthias

Begin forwarded message:

> From: pre@aps.org
> Date: 2. März 2011 17:50:28 MEZ
> To: matthias.schmidt@uni-bayreuth.de
> Subject: Your_manuscript EA10780 Dwandaru
> Reply-To: pre@aps.org
>
> Re: EA10780
> Variational principle of classical density functional theory via
> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
>
> Dear Dr. Schmidt,
>

> The above manuscript has been reviewed by two of our referees.
> Comments from the reports appear below.
>
> The comments of the first referee suggest that considerable revision
> of your paper may be in order. If you resubmit your manuscript, please
> include a summary of the changes made and a brief response to all
> recommendations or criticisms.
>
> Yours sincerely,
>
> Dirk Jan Bukman
> Managing Editor
> Physical Review E
> Email: pre@ridge.aps.org
> Fax: 631-591-4141
> http://pre.aps.org/
>
>
> Code EA10780 Author Dwandaru
>
> Title Variational principle of classical density functional theory
> via Levy's constrained search method
>
> The Editors consider the following section of Physical Review E as
> most appropriate:
>
> Statistical physics
>
> The above paper has been given the following Physics and Astronomy
> Classification Scheme (PACS) index numbers:
>
> 64.10.+h 61.20.Gy 05.20.Jj
>
> If you disagree strongly with our classification, or believe that an
> important PACS number is missing, please let us know. Note that the
> first PACS category listed is taken to be the principal category and
> should correspond with the selected section. The order of the
> remaining categories is not significant. No more than four PACS
> numbers are allowed.
>
> Complete PACS listings may be accessed via the World Wide Web,
> using the following URL: http://publish.aps.org/PACS/pacsgen.html
>
> ---
> Report of the First Referee -- EA10780/Dwandaru

> ---
>
> This paper describes an alternative formulation of classical Density Functional
> Theory. The key point is that the authors do not assume the property they call
> "v-representability" of the density. A consequence is that they are able to
> formulate a dft for the canonical ensemble. I think this paper contains some
> interesting ideas, but I cannot recommend it for publication in PRE in its
> present form as it raises more questions than it answers (as explained below).
> If the authors would address these points, I think the paper could be made
> suitable for PRE.
>
> 1. The first issue that I find unclear is why v-representability of the density
> is such a problem? The authors state in the fourth paragraph of the Introduction
> that v-representability has in fact been proven for classical systems that do
> not include hard-sphere interactions. Although this is a qualified statement,
> the hard-sphere interaction can always be viewed as the limit of a family of
> continuous, non-hard-sphere interactions so that this restriction seems
> relatively mild. (And, of course, real potentials are not truely hard-core in
> nature.) Thus, the repeated emphasis throughout the paper on avoiding the
> assumption of v-representability seems unnecessary.
>
> 2. It is also unclear why, after assuming v-representability, one could not
> follow the Mermin-Evans argument for the canonical ensemble since everything is
> basically just a development of the Gibbs inequality. Why is the alternative
> Levy formulation even necessary for classical systems?
>
> 3. The most important question that is not addressed concerns the utility of the
> results. We know from several studies, many of which are referenced in the
> manuscript, that one cannot generate the correct canonical density distribution
> for small systems simply by minimizing a mean-field free energy functional
> under the constraint of constant particle number. Why not? Where is the
> assumption that one is in the grand canonical, rather than the canonical,
> ensemble critical in the formulation of practical dft models? For example, the
> next step in the development of the formalism is the relation between the
> functional derivatives of the Helmholtz free energy functional and the direct
> correlation functions leading to a general expansion of the helmholtz functional
> about equilibrium. Is there any difficulty in extending this expansion to the
> canonical ensemble (aside from the fact that it is based on taking derivatives
> with respect to the potential and, hence, to the assumption of
> v-representability)? Or, is the only practical problem that the exact and
> semi-exact hard-sphere results used to formulate, e.g. FMT, are explicitly
> formulated for the grand ensemble and so cannot be used as a basis for
> approximating the canonical helmholtz free energy functional?
>
> In summary, I think that the developments in this paper are interesting but

> that, in order to be of interest to more than a very specialized audience, it is
> necessary to say something specific about the implications for practical
> calculations.
>
> ---
> Report of the Second Referee -- EA10780/Dwandaru
> ---
>
> In this paper, the authors extend Levy's functional for electronic
> structure to classical systems. The new functional is based on a
> weaker condition than v-representability of the trial density, but
> recovers the ortodox functional if the constrained search is
> restricted to v-representable one-body densities. The major
> accomplishment of the formal extension to classical systems is the
> definition of the intrinsic free energy functional as clearly
> independent of the external potential. This thoughtful work certainly
> provides a new insight into the foundation of classical DFT, even if
> it is not easy to figure out how the new framework could practically
> be of help in the construction of new free energy functionals (this is
> also recognised by the authors). Further extensions of the formalism
> to quenched-annealed systems are possible and already envisaged as the
> subject of future work. In summary, this is a neat, well-written
> paper, which is enjoyable to read and, according to my opinion, worth
> of publication on the Physical Review E.
>

response for referee A

From: Brams Dwandaru (wipsarian@yahoo.com)

To: matthias.schmidt@uni-bayreuth.de

Date: Friday, 4 March 2011, 06:08 GMT+7

Dear Matthias,

Thank you very much for your email.

I read what you think first and then I read the referees comments.

Yes, Referee B clearly liked our paper.

But like you said, probably referee A did not get our message. I read the report a couple of times. I think the comments by referee A are interesting. And I think we should definitely-positivey give some response to these-I know we can answer these comments. I like challenges. I am giving some thoughts as we speak.

If you are not eager to go through the comments, that is fine. I can certainly do it for us.

I will get in touch as soon as possible.

If you have anything more to say please let me know. I hope you are fine and well.

Best regards
Brams

--- On **Thu, 3/3/11, Matthias Schmidt *<matthias.schmidt@uni-bayreuth.de>*** wrote:

> From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
> Subject: Fwd: Your_manuscript EA10780 Dwandaru

To: "Brams Dwandaru" <wipsarian@yahoo.com>
Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
Date: Thursday, 3 March, 2011, 15:48

Dear Brams,

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Referee A did not get our message and we have to explain to him what our paper is about. Referee B is very nice and say kind things! Clearly Referee B liked our paper.

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All the best,
Matthias

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> From: pre@aps.org
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> Reply-To: pre@aps.org
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> Re: EA10780
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> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
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> The comments of the first referee suggest that considerable revision
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>
> Yours sincerely,
>
> Dirk Jan Bukman
> Managing Editor
> Physical Review E
> Email: pre@ridge.aps.org
> Fax: 631-591-4141
> http://pre.aps.org/
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>
> Code EA10780 Author Dwandaru
>
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>
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> Report of the First Referee -- EA10780/Dwandaru
> ---
>
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> continuous, non-hard-sphere interactions so that this restriction seems
> relatively mild. (And, of course, real potentials are not truely hard-core in
> nature.) Thus, the repeated emphasis throughout the paper on avoiding the
> assumption of v-representability seems unnecessary.
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> 2. It is also unclear why, after assuming v-representability, one could not
> follow the Mermin-Evans argument for the canonical ensemble since everything is
> basically just a development of the Gibbs inequality. Why is the alternative
> Levy formulation even necessary for classical systems?
>
> 3. The most important question that is not addressed concerns the utility of the
> results. We know from several studies, many of which are referenced in the
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> for small systems simply by minimizing a mean-field free energy functional
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> about equilibrium. Is there any difficulty in extending this expansion to the
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> v-representability)? Or, is the only practical problem that the exact and
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>
> In summary, I think that the developments in this paper are interesting but
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> calculations.
>
> ---
> Report of the Second Referee -- EA10780/Dwandaru
> ---
>
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> recovers the ortodox functional if the constrained search is
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> definition of the intrinsic free energy functional as clearly
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> subject of future work. In summary, this is a neat, well-written
> paper, which is enjoyable to read and, according to my opinion, worth
> of publication on the Physical Review E.
>

Your_manuscript EA10780 Dwandaru (response to referee A)

From: Brams Dwandaru (wipsarian@yahoo.com)

To: matthias.schmidt@uni-bayreuth.de

Cc: wipsarian@yahoo.com

Date: Wednesday, 16 March 2011, 06:35 GMT+7

Dear Matthias,

I hope you are fine and well.

I've written some comments concerning the report from referee A.

Please read these comments. Let me know what you think.

I really hope that we're not giving up and can resubmit this article.

Best regards,
Brams

---

1. The first issue that I find unclear is why v-representability of the density is such a problem? The authors state in the fourth paragraph of the Introduction that v-representability has in fact been proven for classical systems that do not include hard-sphere interactions. Although this is a qualified statement, the hard-sphere interaction can always be viewed as the limit of a family of continuous, non-hard-sphere interactions so that this restriction seems relatively mild. (And, of course, real potentials are not truely hard-core in nature.) Thus, the repeated emphasis throughout the paper on avoiding the assumption of v-representability seems unnecessary.

Comments:
Here the referee seems to misunderstood our purpose. He asked why v-reprsentability is a problem and thus avoiding it seems unnecessary.

However, we don't have any problem with v-representability, and therefore, I think, we are not avoiding it. This property comes naturally from the original derivation of Hohenberg-Kohn and thus in the Mermin-Evans derivation. In the Mermin-Evans derivation, especially in the 1979 Adv. Phys. article, this condition is implicit (not stated explicitly). In the contrary, Levy's derivation provides a relaxation to v-representability. And thus, when we derive Levy's method for classical DFT, it is natural that we may relax the v-representability condition.

---

2. It is also unclear why, after assuming v-representability, one could not follow the Mermin-Evans argument for the canonical ensemble since everything is basically just a development of the Gibbs inequality. Why is the alternative Levy formulation even necessary for classical systems?

Comments:
Here, the referee is asking why one could not follow the Mermin-Evans argument for canonical ensemble after assuming v-representability. Then he jumps to an unrelated (I think) to the necessity of Levy's formulation in classical systems.

As stated in the article, Levy's formulation in classical DFT gives a new perspective of defining the intrinsic free energy functional without involving the external potential, which should be the case for any classical system. We do not need to go through Mermin-Evans argument to justify the aforementioned functional, but rather follow a concept which looks more like a variational principle (rather than a chain of dependency argument). The Mermin-Evans and the original Hohenberg-Kohn theorems do not tell us how to actually do the minimization principle, whereas Levy's method directly uses a minimization procedure.

But again we do not have any problem with Mermin-Evans argument as Levy's method retains again v-representability if the one-particle density is v-representable.

Both Mermin-Evans and Levy's methods are developed form the Gibbs inequality. There is (I think) a more subtle argument for canonical DFT using the Mermin-Evans argument, which may be avoided using Levy's formulation. But anyway we use Levy's method because it is an alternative to the former and more straightforward.
---

3. The most important question that is not addressed concerns the utility of the results. We know from several studies, many of which are referenced in the manuscript, that one cannot generate the correct canonical density distribution for small systems simply by minimizing a mean-field free energy functional under the constraint of constant particle number. Why not? Where is the assumption that one is in the grand canonical, rather than the canonical, ensemble critical in the formulation of practical dft models? For example, the

next step in the development of the formalism is the relation between the functional derivatives of the Helmholtz free energy functional and the direct correlation functions leading to a general expansion of the helmholtz functional about equilibrium. Is there any difficulty in extending this expansion to the canonical ensemble (aside from the fact that it is based on taking derivatives with respect to the potential and, hence, to the assumption of v-representability)? Or, is the only practical problem that the exact and semi-exact hard-sphere results used to formulate, e.g. FMT, are explicitly formulated for the grand ensemble and so cannot be used as a basis for approximating the canonical helmholtz free energy functional?

Comments:

Finally, in this third point the referee is asking about the utility of the result. But then he raised a question why one cannot generate the correct canonical density distribution for small systems simply by minimizing a mean-field free energy functional.

In my opinion this is not our problem yet (or it is?). I don't think this article is inteded to answer the question. As this is an ongoing investigation, we may address this in subsequent articles.

--- On **Thu, 3/3/11, Matthias Schmidt *<matthias.schmidt@uni-bayreuth.de>*** wrote:

> From: Matthias Schmidt <matthias.schmidt@uni-bayreuth.de>
> Subject: Fwd: Your_manuscript EA10780 Dwandaru
> To: "Brams Dwandaru" <wipsarian@yahoo.com>
> Cc: "Matthias Schmidt" <matthias.schmidt@uni-bayreuth.de>
> Date: Thursday, 3 March, 2011, 15:48
>
> Dear Brams,
>
> please see below the email that I received from Phys.Rev.E about our paper. Maybe you want to go scroll down and first read what the referees say, before you go on reading what I think?
>
> Plase scroll down!
>
> Referee A did not get our message and we have to explain to him what our paper is about. Referee B is very nice and say kind things! Clearly Referee B liked our paper.

We will try and "fight" Referee A and convince him to make a positive judgment. This requires some thought on our side. I have to say that I am not very eager to go into all the details that he lays out in his report. Let us see, please read the reports carefully.

All the best,
Matthias

Begin forwarded message:

> From: pre@aps.org
> Date: 2. März 2011 17:50:28 MEZ
> To: matthias.schmidt@uni-bayreuth.de
> Subject: Your_manuscript EA10780 Dwandaru
> Reply-To: pre@aps.org
>
> Re: EA10780
> Variational principle of classical density functional theory via
> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
>
> Dear Dr. Schmidt,
>
> The above manuscript has been reviewed by two of our referees.
> Comments from the reports appear below.
>
> The comments of the first referee suggest that considerable revision
> of your paper may be in order. If you resubmit your manuscript, please
> include a summary of the changes made and a brief response to all
> recommendations or criticisms.
>
> Yours sincerely,
>
> Dirk Jan Bukman
> Managing Editor
> Physical Review E
> Email: pre@ridge.aps.org

> Fax: 631-591-4141
> http://pre.aps.org/
>
>
> Code EA10780 Author Dwandaru
>
> Title Variational principle of classical density functional theory
> via Levy's constrained search method
>
> The Editors consider the following section of Physical Review E as
> most appropriate:
>
> Statistical physics
>
> The above paper has been given the following Physics and Astronomy
> Classification Scheme (PACS) index numbers:
>
> 64.10.+h 61.20.Gy 05.20.Jj
>
> If you disagree strongly with our classification, or believe that an
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>
> Complete PACS listings may be accessed via the World Wide Web,
> using the following URL: http://publish.aps.org/PACS/pacsgen.html
>
> ---
> Report of the First Referee -- EA10780/Dwandaru
> ---
>
> This paper describes an alternative formulation of classical Density Functional
> Theory. The key point is that the authors do not assume the property they call
> "v-representability" of the density. A consequence is that they are able to
> formulate a dft for the canonical ensemble. I think this paper contains some

> interesting ideas, but I cannot recommend it for publication in PRE in its
> present form as it raises more questions than it answers (as explained below).
> If the authors would address these points, I think the paper could be made
> suitable for PRE.
>
> 1. The first issue that I find unclear is why v-representability of the density
> is such a problem? The authors state in the fourth paragraph of the Introduction
> that v-representability has in fact been proven for classical systems that do
> not include hard-sphere interactions. Although this is a qualified statement,
> the hard-sphere interaction can always be viewed as the limit of a family of
> continuous, non-hard-sphere interactions so that this restriction seems
> relatively mild. (And, of course, real potentials are not truely hard-core in
> nature.) Thus, the repeated emphasis throughout the paper on avoiding the
> assumption of v-representability seems unnecessary.
>
> 2. It is also unclear why, after assuming v-representability, one could not
> follow the Mermin-Evans argument for the canonical ensemble since everything is
> basically just a development of the Gibbs inequality. Why is the alternative
> Levy formulation even necessary for classical systems?
>
> 3. The most important question that is not addressed concerns the utility of the
> results. We know from several studies, many of which are referenced in the
> manuscript, that one cannot generate the correct canonical density distribution
> for small systems simply by minimizing a mean-field free energy functional
> under the constraint of constant particle number. Why not? Where is the
> assumption that one is in the grand canonical, rather than the canonical,
> ensemble critical in the formulation of practical dft models? For example, the
> next step in the development of the formalism is the relation between the
> functional derivatives of the Helmholtz free energy functional and the direct
> correlation functions leading to a general expansion of the helmholtz functional
> about equilibrium. Is there any difficulty in extending this expansion to the
> canonical ensemble (aside from the fact that it is based on taking derivatives
> with respect to the potential and, hence, to the assumption of
> v-representability)? Or, is the only practical problem that the exact and
> semi-exact hard-sphere results used to formulate, e.g. FMT, are explicitly
> formulated for the grand ensemble and so cannot be used as a basis for
> approximating the canonical helmholtz free energy functional?

> In summary, I think that the developments in this paper are interesting but
> that, in order to be of interest to more than a very specialized audience, it is
> necessary to say something specific about the implications for practical
> calculations.
>
> ---
> Report of the Second Referee -- EA10780/Dwandaru
> ---
>
> In this paper, the authors extend Levy's functional for electronic
> structure to classical systems. The new functional is based on a
> weaker condition than v-representability of the trial density, but
> recovers the ortodox functional if the constrained search is
> restricted to v-representable one-body densities. The major
> accomplishment of the formal extension to classical systems is the
> definition of the intrinsic free energy functional as clearly
> independent of the external potential. This thoughtful work certainly
> provides a new insight into the foundation of classical DFT, even if
> it is not easy to figure out how the new framework could practically
> be of help in the construction of new free energy functionals (this is
> also recognised by the authors). Further extensions of the formalism
> to quenched-annealed systems are possible and already envisaged as the
> subject of future work. In summary, this is a neat, well-written
> paper, which is enjoyable to read and, according to my opinion, worth
> of publication on the Physical Review E.
>

Fwd: [Web] resub EA10780 Dwandaru

From: Matthias Schmidt (matthias.schmidt@uni-bayreuth.de)

To: wipsarian@yahoo.com

Cc: matthias.schmidt@uni-bayreuth.de

Date: Friday, 15 April 2011, 19:43 GMT+7

Dear Brams,

I forward the email from PRE below. Just formalities, the status page on
the web was also updated (copied below). Probably they will send it
to the referee again - we will have to be patient for a few more weeks.
I hope I will find time to start to work on our dynamics paper again!

All the best,
Matthias

CURRENT STATUS OF MANUSCRIPT:
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15Apr11 Correspondence (miscellaneous) sent to author
02Mar11 15Apr11 Ed. decision and/or ref. comments to author; response rcvd
25Jan11 27Feb11 Review request to referee; report received
15Feb11 16Feb11 Reminder to referee; response received
25Jan11 14Feb11 Review request to referee; report received
20Jan11 Acknowledgment sent to author
19Jan11 Correspondence (miscellaneous) sent to author
19Jan11 Right to publish signature received

Begin forwarded message:

> From: esub-adm@aps.org
> Date: 15. April 2011 13:48:44 MESZ
> To: pretex@ridge.aps.org
> Cc: matthias.schmidt@uni-bayreuth.de
> Subject: [Web] resub EA10780 Dwandaru
>
> Subject: EA10780
>
> Manuscript code: EA10780
> RECVD: Fri Apr 15 07:48:44 2011
> Resubmission to: Physical Review E
> Resubmission type: resubmit
>
>
> Replaced files:
> levy.tex 04-15-2011
>
> Details of changes:
> Re: EA10780
> Variational principle of classical density functional theory via
> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
>
> Dear Dr. Bukman,
>
> thank you for your email and for sending us the Referee Reports for
> the above paper. We thank both Referees for their reports. We are
> delighted by the very positive judgement of the Second Referee. We
> have addressed the constructive criticism raised by the First
> Referee. Please find our response to the First Referee and the revised
> manuscript enclosed in this resubmission. We look forward to
> publication of our manuscript in Physical Review E.
>
> Yours sincerely,
> Matthias Schmidt and Brams Dwandaru
>
>
> Reply to the First Referee
> ==========
>
> We thank the Referee for a very careful reading of our our paper and
> for his/her thoughtful report that raises several important points. A

> detailed response to these points is given below. We emphasize firstly
> that our paper provides only an alternative to the standard
> (Mermin-Evans) derivation of the variational principle. Hence it does
> not invalidate in any way the standard derivation of DFT, or any of
> its implicit assumptions, such as v-representability. Secondly, we are
> only concerned with the formulation of the DFT principles, not with
> constructing explicit approximations for the excess free energy
> functional itself, which constitutes a challenging topic in
> itself. These two points could lead (or may have led) to potential
> confusion. We revised the manuscript in order to avoid such
> confusion, as laid out in the following.
>
> 1. We agree that whether or not relying on v-representability is
> merely a conceptual issue and that there is no problem with using
> it. On the other hand, the proof of v-representability by Chayes,
> Chayes, and Lieb (Ref.[20]) is a very involved piece of
> work. Furthermore, while we do not disagree with the Referee's
> discussion of hard sphere potentials, we feel that this is rather
> based on intuition than on rigorous arguments (one needed to avoid
> configurations with local packing fractions beyond close packing -
> which can occur for continuous potentials). One can avoid such
> subtleties by relaxing to f-representability. Hence the emphasis in
> the paper on representability does not stem from practical
> implications for carrying out actual calculations, but rather to
> highlight the conceptual differences between Levy's and Mermin-Evans'
> methods.
>
> We clarify this situation by adding to the Introduction the following
> text (see p.3).
>
> "[We refer to this condition as f-representability of a given rho.]
> While distinguishing between the different type of representability
> in practical DFT calculations seems unnecessary, we find the
> discrimination very useful for conceptual purposes and hence point
> out throughout the manuscript which of the conventions is followed
> in the reasoning."
>
> 2. The significance of the Levy formulation for classical DFT is that
> it provides an alternative to the Mermin-Evans argument. We think that
> such an alternative can constitute an important, or at least
> interesting, further foundation of classical DFT. Note that Levy's
> 1979 PNAS paper is very well famous in the electronic structure
> community (counting 780 citations at present). This gives further
> justification to introducing the liquid state community to Levy's
> ideas. Note that this situation is already described in the paper

> (p.2)
>
> "Kohn adopted the constrained search for his Nobel lecture [13],
> and it is viewed as an important theoretical contribution to the
> foundation of DFT for electronic structure."
>
>
>
> 3. The question of how to obtain actual (approximative) computational
> schemes in DFT, in particular in canonical DFT, is a very important
> one. The Referee lays out very clearly the corresponding pitfalls and
> intricacies. The fact that this constitutes a very demanding task is
> one of the reasons why we refrain from trying to formulate any
> explicit DFT approximations in the present paper. We are solely
> concerned with the mathematics of laying out the variational
> principle, following Levy's arguments. We now describe this purpose
> more explicitly in the Introduction of the revised manuscript as
> follows (end of p.3).
>
> "[Several relatively recent contributions address the problem of
> formulating DFT in the canonical ensemble [21-26].] The authors of
> these papers consider the important problem of how to obtain DFT
> approximations that make computations in the canonical ensemble
> feasible. Our present article has a much lower goal: We are only
> concerned with formulating the variational principle in an
> alternative way."
>
> In the conclusions we have clarified the relationship of our work to
> the literature as follows (p.15).
>
> "[Hence, whether the definition (22) helps to construct]
> approximations for grand-canonical free energy functionals remains
> an open question. For the case of the canonical ensemble we point
> the reader to the very significant body of work that has been
> carried out to formulate a computational scheme that permits to
> capture the effects that arise due to the constraint of fixed
> number of particles [21-26]."
>
> Considering what the Levy formulation implies for functional
> derivatives of the Helmholtz free energy functional and the direct
> correlation functions is an interesting topic. We feel, however, that
> this goes beyond the scope of the present work - which is already a
> quite dense manuscript.

Fwd: Acceptance EA10780 Dwandaru

From: Matthias Schmidt (matthias.schmidt@uni-bayreuth.de)

To: wipsarian@yahoo.com

Cc: matthias.schmidt@uni-bayreuth.de

Date: Wednesday, 20 April 2011, 13:38 GMT+7

Dear Brams,

please find below the email about acceptance of our paper.
So it is definitive! Congratulations again; this is a piece
of work to be proud of!

All the best,
Matthias

Begin forwarded message:

> From: pre@aps.org
> Date: 19. April 2011 13:07:27 MESZ
> To: matthias.schmidt@uni-bayreuth.de
> Subject: Acceptance EA10780 Dwandaru
> Reply-To: pre@aps.org
>
> Re: EA10780
> Variational principle of classical density-functional theory via
> Levy's constrained search method
> by Wipsar Sunu Brams Dwandaru and Matthias Schmidt
>
> Dear Dr. Schmidt,
>
> We are pleased to inform you that your manuscript has been accepted
> for publication as a Regular Article in Physical Review E.
>
> Your manuscript will now be prepared for the production process. If
> any issues arise we will contact you, otherwise your manuscript will
> be forwarded directly to our production department. Please do not

> send a revised manuscript or figures at this time unless requested.
>
> Yours sincerely,
>
> Gary S. Grest
> Editor
> Physical Review E
> Email: pre@ridge.aps.org
> Fax: 631-591-4141
> http://pre.aps.org/
>
>
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> Submit your summary as soon as possible to allow time to consider and
> if appropriate produce the story before your paper is published.
>
> Summary submission instructions: http://authors.aps.org/publicity.html
>
> Thank you for your cooperation.
>