University of Groningen

An improved upper bound for the free energy of a single chain lattice model

Brinke, G. ten; Karasz, F. E.

Published in:
The Journal of Chemical Physics

DOI:
[10.1063/1.444771](https://doi.org/10.1063/1.444771)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1983

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Brinke, G. T., & Karasz, F. E. (1983). An improved upper bound for the free energy of a single chain lattice model. *The Journal of Chemical Physics*, 78(2), 995-996. <https://doi.org/10.1063/1.444771>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

- ¹C. S. Choi, H. J. Prask, and E. Prince, *J. Chem. Phys.* **61**, 3523 (1974).
- ²M. Prager and B. Alefeld, *J. Chem. Phys.* **65**, 4927 (1976).
- ³M. Prager, B. Alefeld, and A. Heidemann, in *Magnetic Resonances and Related Phenomena*, Proceedings of the XIXth Congress, Ampere, Groupement Ampere, Heidelberg, Geneva, 1976, p. 389.
- ⁴M. Prager and W. Press, *J. Chem. Phys.* **75**, 494 (1981).
- ⁵K. Maki, *J. Chem. Phys.* **74**, 2049 (1981).
- ⁶K. J. Lushington, K. Maki, J. A. Morrison, A. Heidemann, and W. Press, *J. Chem. Phys.* **75**, 4010 (1981).
- ⁷A. Hüller and J. C. Raich, *J. Chem. Phys.* **71**, 3853 (1979).
- ⁸M. Trefler and G. R. Wilkinson, *Discuss. Faraday Soc.* **48**, 108 (1969).

Kasteleyn's^{3,4} analytic solution for Hamiltonian walks on a square lattice oriented according to the Manhattan traffic rule. Briefly, this rule states that the orientations along the successive rows and columns alternate like the alternating one-way streets in force in Manhattan.

The exact solution of Kasteleyn for the free energy per lattice site of a single chain on a square lattice with the Manhattan constraint is given by

$$f_{MH}(T) = \frac{-kT}{(2\pi)^2} \int_0^\pi dw_1 \int_0^\pi dw_2 \ln 4(z_1^4 \sin^2 w_1 + z_2^4 \sin^2 w_2), \quad (2)$$

where z_1 and z_2 are the weights of the horizontal and vertical bonds, respectively. This model deviates from the one studied by Gujrati and Goldstein not only by the Manhattan constraint but also by the way in which weights are assigned to the various bonds. It nevertheless leads to an upper bound for the free energy of the model of interest. To see this we note that every horizontal (or vertical) bond corresponds to at most two *gauche* bonds (see Fig. 1). Equation (2) therefore gives an upperbound $\tilde{f}_{MH}(T)$ for $f_H(T)$ if we take $z_1 = \exp(-2\epsilon/kT)$ and $z_2 = 1$:

$$\begin{aligned} \tilde{f}_{MH}(T) &= \frac{-kT}{(2\pi)^2} \int_0^\pi dw_1 \int_0^\pi dw_2 \ln 4[\exp(-8\epsilon/kT) \sin^2 w_1 + \sin^2 w_2] \\ &= \frac{-4kT}{(2\pi)^2} \int_0^1 \frac{dx}{\sqrt{1-x^2}} \int_0^1 \frac{dy}{\sqrt{1-y^2}} \ln 4[\exp(-8\epsilon/kT)x^2 + y^2] \\ &= \frac{-kT}{\pi} \int_0^1 \frac{dx}{\sqrt{1-x^2}} \ln[\exp(-4\epsilon/kT)x \\ &\quad + \sqrt{\exp(-8\epsilon/kT)x^2 + 1}] \quad (3) \end{aligned}$$

From this expression it follows simply that the low temperature approximation for the upper bound is given by

$$\tilde{f}_{MH}(T) \approx \frac{-kT}{\pi} \exp(-4\epsilon/kT). \quad (4)$$

This result is slightly better but very similar to the result of Gujrati and Goldstein mentioned before.

To understand this similarity we note first that Gordon *et al.*⁶ have argued that the Manhattan traffic regulation is not an essential constraint. According to their results it is not unlikely that the number of Hamiltonian walks of length N on a square lattice with or without the Manhattan constraint is asymptotically equal to 1.338^N for large N . Moreover, all the conformations taken into account by Gujrati and Goldstein² that satisfy the Manhattan constraint are also counted with the correct Boltzmann factor in the construction of our upper bound.

This work was supported by AFOSR Grant 81-0101.

¹P. D. Gujrati, J. Phys. A 13, L437 (1980).

²P. D. Gujrati and M. Goldstein, J. Chem. Phys. 74, 2596 (1981).

³P. W. Kasteleyn, Physica 29, 1329 (1963).

⁴P. W. Kasteleyn, in *Graph Theory and Theoretical Physics*, edited by F. Harary (Academic, New York, 1967).

⁵P. J. Flory, Proc. R. Soc. London Ser. A 234, 60 (1956).

⁶M. Gordon, P. Kapadio, and A. Malakis, J. Phys. A 9, 751 (1976).

On representation of electron-electron repulsion energies by simple one-electron functionals

Shridhar R. Gadre and Rajeev D. Bendale

Department of Chemistry, University of Poona, Pune 411 007, India
(Received 5 January 1982; accepted 29 January 1982)

The treatment of electron-electron repulsion energies is the bottleneck of quantum chemical calculations on atomic and molecular systems. In recent publications, bounds to the Coulomb^{1,2} and exchange³ components of the electron repulsion energy have been obtained in terms of simple one-electron functionals. Parr, Gadre, and Bartolotti⁴ developed a local density functional model in which the total electron-electron repulsion energy was represented as $V_{ee} = 0.754 N^{2/3} \int \rho^{4/3} d\tau$, where N is the number of the electrons in the system and $\rho(r)$, the electron density. This model yields reasonable values of total energies, and components thereof, and also fair estimates of $\langle r^{-n} \rangle$ expectation

values. Gadre and Pathak⁵ used the bound in Ref. 2 to carry out calculations of the helium atom and the hydrogen molecule using simple wave functions. Typical errors in their energies, from the corresponding variational ones obtained by an accurate representation of V_{ee} , were 2%. The equilibrium distance in the case of H_2 turned out to be quite accurate (error $\sim 1\%$). The force constant was also predicted correctly to within 2%. With this encouraging experience, the representation of the Coulomb energies (J) and the electron-electron repulsion energies (V_{ee}) seemed to us a worthwhile project to embark upon. Here, we present the results of our analysis of the various func-