AD-A164 377 DISCONTINUITY OF THE EXCHANGE CORRELATION POTENTIAL FROM A DENSITY FUNCTIONAL VIEWPOINT(U) CALIFORNIA UNIV SANTA BARBARA DEPT OF PHYSICS W KOHN 10 FEB 86 TR-5 1/1

UNCLASSIFIED N00014-84-K-0548 F/G 20/3 NL

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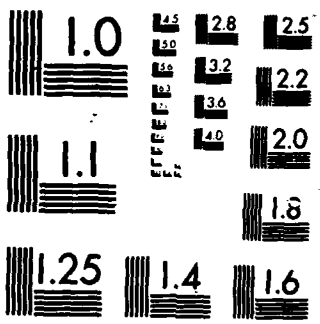

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OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0548

Task No. NR372-160

TECHNICAL REPORT NO. 5

Discontinuity of the exchange correlation potential from a density functional view point

by

W. Kohn

Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

The calculation of energy gaps of insulators is an important theory objective. A commonly used method is density functional theory. Recently it was shown that an unexpected difficulty (discontinuity of the exchange correlation potential) arises. This paper makes a contribution towards the understanding of this problem.

February 1986

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Prepared for publication

in

Physical Review B, Rapid Publications (1986)

Department of Physics

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Santa Barbara, CA 93106

February 1986

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
TECHNICAL REPORT 5

2. GOVT ACCESSION NO.
AD-A164 979

3. RECIPIENT'S CATALOG NUMBER
N00014-01

4. TITLE (and Subtitle)
Discontinuity of the exchange correlation potential from a density functional view point.

5. TYPE OF REPORT & PERIOD COVERED
TECHNICAL REPORT
6/85-12/85

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
W. Kohn

8. CONTRACT OR GRANT NUMBER(s)
N00014-84-K-0548

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of California
Physics Department, Santa Barbara, CA 93106
See:Contracts & Grants-Room 3227 Cheadle

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
TASK NO. NR372-160

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Research
Electronics & Solid State Physics Program
800 N. Quincy, Arlington, VA 22217

12. REPORT DATE
February 10, 1986

13. NUMBER OF PAGES
4

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Office of Naval Research Detachment
1030 East Green Street
Pasadena, CA 91106

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
"Approved for Public Release: Distribution Unlimited"

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
Reports Distribution List for ONR Physics Division Office - Unclassified Contracts

18. SUPPLEMENTARY NOTES
Accepted for publication in Physical Review B, Rapid Publications (1986)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Exchange correlation potential; density functional theory; insulators;

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An expression for the discontinuity of the exchange correlation potential v_{xc} of an insulator is derived entirely within the framework of density functional theory. The discontinuity is expressed in terms of changes of the exchange correlation energy E_{xc}, of a perfect N-particle insulator when (a) a conduction electron is introduced (b) a valence electron is

removed and (c) an external perturbation is applied to the perfect insulator (without changing N) such that the density change is equal to minus the sum of the density changes in (a) and (b).

Discontinuity of the Exchange Correlation Potential from a Density Functional View Point

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Abstract

An expression for the discontinuity of the exchange correlation potential v_{xc} of an insulator is derived entirely within the framework of density functional theory. The discontinuity is expressed in terms of changes of the exchange correlation energy, E_{xc}, of a perfect N-particle insulator when (a) a conduction electron is introduced (b) a valence electron is removed and (c) ~~the~~ an external perturbation is applied to the perfect insulator (without changing N) such that the density change is equal to minus the sum of the density changes in (a) and (b).

Since the work of Perdew and Levy[1] and of Sham and Schlüter[2] it has been known that the exchange correlation potential $v_{xc}(r)$ of the Kohn-Sham (KS) equations[3] has an r-independent discontinuity Δ, as one crosses the energy gap. This discontinuity has been studied with the aid of Green's function theory by Wang and Pickett[4], Sham and coworkers[2,5,6,7] and Hanke[8]. In this note we discuss the discontinuity entirely from a density functional view point.

We shall consider an insulator at temperature $T=0^+K$ in three physical ground-states: 1. with N electrons, without conduction electrons or holes. We denote the corresponding density distributions by $n_0(r)$ with

$$\int n_0(r)dr = N \quad ; \tag{1}$$

2. with $N+\nu$ electrons; and 3. with $N-\nu$ electrons, with $\nu \ll N$.[9] We write the densities in states 2. and 3. as

$$\begin{aligned} n^+(r) &\equiv n_0(r)+\nu\, n^c(r); \quad \int n^c(r)dr = 1. \\ n^-(r) &\equiv n_0(r)-\nu\, n^v(r); \quad \int n^v(r)dr = 1. \end{aligned} \tag{2}$$

We take (kT) much smaller than any physical energy but larger than the energy spacing between successive single particle excitations.[7] The system is in contact with a particle bath, allowing continuous changes of the total particle number[1].

By its definition, the energy gap can be expressed in terms of ground state energies,

$$E_g \equiv \frac{1}{\nu}\left[(E_{N+\nu}-E_N) - (E_N-E_{N-\nu})\right]. \quad (3)$$

Each of these energy is given, in the KS theory[3], by the expression

$$E_v[n(r)]=T_s[n(r)]+\int v(r)n(r)dr + \tfrac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\,dr\,dr' + E_{xc}[n(r)], \quad (4)$$

where v(r) is the (fixed) external potential and the other symbols have their usual meanings. As is well-known, this expression can be transformed into

$$E_v[n(r)]=\sum\varepsilon_i[n(r)]-\tfrac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}dr\,dr'+E_{xc}[n(r)] - \int v_{xc}(r';[n(r)])n(r')dr' \quad (5)$$

where i runs over all occupied single particle levels associated with the KS equation

$$\left\{-\tfrac{1}{2}\nabla^2+v(r)+\int\frac{n(r')}{|r-r'|}dr'+v_{xc}(r;n[r'])\right\}\psi_i(r)=\varepsilon_i\psi_i(r), \quad (6)$$

and

$$v_{xc}(r;[n(r')]) \equiv \delta E_{xc}[n(r')]/\delta n(r). \quad (7)$$

We have emphasized in our notation that v_{xc} and ε_i are functionals of $n(r')$.

The difference $E_{N+\nu}-E_N$ in (3) can now be calculated from (5), to first order in ν:

$$E_{N+\nu}-E_N = \sum_{N+1}^{N+\nu} \varepsilon_i^c + \sum_{1}^{N} \delta\varepsilon_i^c - \nu\int \frac{n^c(r)n_o(r')}{|r-r'|} dr\, dr'$$

$$+ \delta E_{xc}[n(r)] - \nu \int v_{xc}(r';[n_o(r)]n^c(r')dr' -$$

$$- \int \delta v_{xc}(r';[n(r)])n_o(r')\, dr'$$

$$= \nu\, \varepsilon_{N+1}^c \qquad (8)$$

Here ε_{N+1}^c is the lowest conduction band energy of the KS equation for the N+ν particle system ($\nu\to 0$), calculated with the exchange correlation potential $v_{xc}^c(r)$ appropriate for this system:

$$v_{xc}^c(r) \equiv \lim_{\nu\to 0} \frac{\delta E_{xc}[n_o(r)+\nu n^c(r)]}{\delta n(r)} \qquad (9)$$

The simplification in the last step of Eq. (8) is due to the cancellation of the 2nd, 3rd and last terms, and of the 4th and 5th terms. Similarly

$$E_N - E_{N-\nu} = \nu\, \varepsilon_{N-1}^v \quad , \qquad (10)$$

where ε_{N-1}^v is computed with

$$v_{xc}^v(r) \equiv \lim_{\nu\to 0} \frac{\delta E_{xc}[n_o(r)-\nu n^v(r)]}{\delta n(r)} \quad . \qquad (11)$$

Thus the gap is given by

$$E_g = \varepsilon^c_{N+1} - \varepsilon^v_{N-1} . \tag{12}$$

The arguments of refs. (1) and (2) show, and we shall verify, that

$$v^c_{xc}(r) - v^v_{xc}(r) \equiv \Delta, \tag{13}$$

a constant independent of r. Therefore (12) can also be written as

$$E_g = \varepsilon^v_{N+1} - \varepsilon^v_{N-1} + \Delta$$

$$= \varepsilon^c_{N+1} - \varepsilon^c_{N-1} + \Delta = \varepsilon_g + \Delta , \tag{14}$$

where ε_g is the non-physical gap of the KS single particle insulator, computed with either v^v_{xc} or v^c_{xc}.

We now turn to a consideration of v^c_{xc}, Eq. (9). We introduce

$$\delta n_{r'}(r) = \gamma\ \delta(r-r') \quad , \quad \int \delta(r-r')\ dr = 1 \tag{15}$$

where $\gamma \ll 1$ and δ is a normalized, regularized δ-function.

Then

$$v^{c}_{xc}(r') = \lim_{\nu\to 0} \lim_{\gamma\to 0} \frac{1}{\gamma}\{E_{xc}[n_{o}(r)+\nu\, n^{c}(r)+\gamma\delta(r-r')] - \tag{16}$$

$$-E_{xc}[n^{o}(r)+\nu n^{c}(r)]\}$$

It is now useful to decompose $\delta(r-r')$ into two parts: $n^{c}(r)$, which increases the number of electrons by 1, and a remainder, $m^{c}_{r'}(r)$, which leaves the number of electrons unchanged at N.

$$\delta(r-r') = n^{c}(r) + m^{c}_{r'}(r), \tag{17}$$

where, evidently in view of Eqs. (2) and (15),

$$\int m^{c}_{r'}(r)dr = \int[\delta(r-r') - n^{c}(r)]dr = 0. \tag{18}$$

Substituting (17) into (16) gives two terms,

$$v^{c}_{xc}(r') = \mu^{c}_{xc} + w^{c}_{xc}(r') \quad , \tag{19}$$

where

$$\mu^{c}_{xc} \equiv E_{xc}[n_{o}(r) + n^{c}(r)] - E_{xc}[n_{o}(r)] \tag{20}$$

$$\equiv E_{xc,N+1} - E_{xc,N}$$

and

$$w^{c}_{xc}(r') = \lim_{\nu\to 0}\lim_{\gamma\to 0}\frac{1}{\gamma}\{E_{xc}[n_0(r)+\nu n^{c}(r)+\gamma m^{c}_{r'}(r)]-E_{xc}[n_0(r)$$

$$+\ \nu n^{c}(r)]\}. \qquad (21)$$

The two density arguments in Eq. (21) differ by $\gamma\ m^{c}_{r'}(r)$, defined by Eq. (17), and corresponding to $\delta N=0$. This density difference must therefore be understood as being brought about by the action of a small external perturbing potential, $\gamma\ u_{r'}(r)$ modifying the $(N+\nu)$ particle ground state. In the limit $\nu\to 0$ the role of the conduction electrons in (21) becomes negligible, so that

$$w^{c}_{xc}(r') = \lim_{\gamma\to 0}\frac{1}{\gamma}\{E_{xc}[n_0(r)+\gamma m^{c}_{r'}(r)]-E_{xc}[n_0(r)]\}. \qquad (22)$$

In a completely analogous manner we obtain the following results for $v^{v}_{xc}(r')$:

$$v^{v}_{xc}(r') = \mu^{v}_{xc} + w^{v}_{xc}(r') \quad , \qquad (23)$$

where

$$\mu^{v}_{xc} = E_{xc}[n_0(r)] - E_{xc}[n_0(r) - n^{v}(r)] \quad ,$$

$$\equiv E_{xc,N} - E_{xc,N-1}, \qquad (24)$$

and

$$w^{v}_{xc}(r') = \lim_{\gamma\to 0} \frac{1}{\gamma}\{\varepsilon_{xc}[n_0(r)] - E_{xc}[n_0(r) - \gamma m^{v}_{r'}(r)] \quad (25)$$

with

$$m^{v}_{r'}(r) \equiv \delta(r-r') - n^{v}(r). \quad (26)$$

From the expressions (19), (20), (22) and (23), (24), (25) we can calculate the difference, $v^{c}_{xc}-v^{v}_{xc}$. Note that the two particle number <u>conserving</u> changes, (22) and (25), can be combined

$$\{E_{xc}[n_0(r)+\gamma m^{c}_{r'}(r)]-E_{xc}[n_0(r)\}-\{E_{xc}[n_0(r)]$$

$$-E_{xc}[n_0(r)-\gamma m^{v}_{r'}(r)]\}$$

$$= E_{xc}[n_0(r)+\gamma(m^{c}_{r'}(r)-m^{v}_{r'}(r))]-E_{xc}[n_0(r)]$$

$$= E_{xc}[n_0(r)+\gamma(n^{c}(r)-n^{v}(r)]-E_{xc}[n_0(r)], \quad (27)$$

independent of r'. Thus we obtain for the discontinuity of v_{xc},

$$\Delta \equiv v_{xc}^{c}(r') - v_{xc}^{v}(r') = (\mu_{xc}^{c} - \mu_{xc}^{v}) + (w_{xc}^{c}(r') - w_{xc}^{v}(r'))$$

$$= \{E_{xc}[n_0(r) + n^{c}(r)] - E_{xc}[n_0(r)]\} + \{E_{xc}[n_0(r) - n^{v}(r)] - E_{xc}\}$$

$$+ \{E_{xc}[n_0(r) - (n^{c}(r) - n^{v}(r))] - E_{xc}[n_0(r)\}. \qquad (28)$$

These three terms represents the changes in the exchange-correlation energy of the N-particle insulator when (a) a conduction electron is added; (b) a valence electron is removed; and (c) an external potential is applied which changes the density of the N-particle insulator by $-(n^{c}(r) - n^{v}(r))$ without introducing either electrons or holes. Note that _if_ $E_{xc}[n(r)]$ had a regular dependence on $n(r)$ near $n(r) = n_0(r)$, then the three terms could be expanded in the small quantities $n^{c}(r)$ and $n^{v}(r)$ resulting in

$$\Delta_{reg} = \left. \frac{\sigma E_{xc}[n(r')]}{\sigma n(r)} \right|_{n(r)=n_v} x \; \{n^{c}(r) - n^{v}(r) - (n^{c}(r) n^{v}(r))\} dr = 0 \qquad (29)$$

Thus any approximate theory which uses a regular expression for E_{xc} - as, for example, the local density approximation - must yield a vanishing Δ. The correct formal expression (28) makes it clear however, on physical grounds, why Δ does not vanish: the effect on E_{xc} of modifying the external potential of the insulator so that its density changes by

$-(n^c(r)-n^v(r))$ does not cancel the sum of the physically totally different changes of adding an electron with density $n^c(r)$ and of removing an electron with density $n^v(r)$. The correct $E_{xc}[n(r)]$ will give the correct Δ by Eq.(28). It remains a challenge to find useful non-regular expressions for E_{xc} which will yield accurate values for Δ.

The support of the National Science Foundation (Grant No. DMR 83-10117) and of the Office of Naval Research (Contract No. N00014-84-K- 0548) are gratefully acknowledged. It is a pleasure to thank Professor H. Bilz for hospitality at the Max Planck Institute for Solid State Research in Stuttgart where this work was completed. Finally I would like to express my special thanks to Dr. W. Hanke for extensive and invaluable discussions.

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9. Effects due to the long range Coulomb repulsion of the ν conduction electrons (or valence holes) are of second order in ν and need not concern us here.

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