THE CHEMICAL POTENTIAL FOR INTERACTING FERMIONS
IN A HARMONIC POTENTIAL

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1. INTRODUCTION

One of the key concepts in density functional theory is the chemical potential. For a fixed Hamiltonian in second-quantized form one may define a sequence of ground state energies $E(N)$ for varying integral number, $N$, of electrons. Although this scheme does not serve to provide a definition of $E(N)$ for non-integral $N$, the chemical potential is usually defined as

$$\mu = \Delta E(N) / \Delta N \quad (1)$$

and evaluated by a polynomial interpolation among the $E(N)$ for nearby values of $N$.

The difficulties inherent in this approach surface in the simplest model of an atom. For 0, 1 and 2 electrons, $E(N)$ may be approximated by

$$E(0) = 0 \quad (2a)$$
$$E(1) = \varepsilon_1 \quad (2b)$$
$$E(2) = 2\varepsilon_1 + J_{11} \quad (2c)$$

where $\varepsilon_1$ is the 1s energy for charge $Z$ and $J_{11}$ is the Coulomb repulsion integral. A polynomial fit of Eqs. (2a-c) yields

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\[ E(N) = \epsilon_1 N + \frac{1}{2} N(N-1)J_{11} \]  

and

\[ \mu = \epsilon_1 + (N-\frac{1}{2})J_{11} \]

for the energy and chemical potential, respectively. Alternatively, \( E \) could have been fit with

\[ E(N) = \epsilon_1 N + N\nu N\nu J_{11} \]

In Eq. (4) the number of spin-up and spin-down electrons is related by

\[ N^+ + N^- = N, \quad 0 \leq N^+ \leq 1, \quad 0 \leq N^- \leq 1 \]

Minimization of \( E \) with respect to \( N^+ \) leads to the following equations for \( E \) and \( \mu \):

\[ E(N) = \epsilon_1 N \quad 0 \leq N \leq 1 \]  
\[ E(N) = \epsilon_1 N + (N-1)J_{11} \quad 1 \leq N \leq 2 \]  
\[ \mu = \epsilon_1 \quad N < 1 \]  
\[ \mu = \epsilon_1 + J_{11} \quad N > 1 \]

Clearly, \( \mu \) is undefined at \( N = 1 \). Similarly, for \( 2 < N < 3 \) one expects

\[ \mu = \epsilon_2 + 2J_{12} - K_{12} \]

Thus, the energy may logically be regarded as piece-wise linear in \( N \) with discontinuities in the slope precisely at the points where \( \mu \) is sought.

Quadratic interpolation between \( E(N) \) and \( E(N \pm 1) \) yields a \( \mu(N) \) which is the average of the slopes of a piecewise linear fit on either side of \( N \). This definition has been used by Parr\(^7\) and March\(^1\text{--}^4\). March\(^1\) has also discussed the results of fitting a higher degree polynomial through more nearby values \( N \pm k \). The results of this approach are limited by the experimental data. March\(^1\) has chosen not to include values of \( E(N + k) \) in the range where the extra electrons are unbound (so that \( E(N + k - 1) = E(N + k) \)).

2. N-BODY HARMONIC OSCILLATOR

Consider the following Hamiltonian for \( N \) indistinguishable, spin one-half, fermions in three dimensions